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# Journal of the Council for Scientific and Industrial Research.

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## The Control of Silverfish and the German Cockroach

*By T. Greaves**

*Summary*

Successful control of silverfish (*Ctenolepisma longicaudata* Esch.) was achieved by the application of 1½-2 lb. of 10 per cent. DDT dust in Canberra houses, each containing six to eight rooms. Using a modified hand dust-gun, 1-1½ lb. was applied to crevices, behind skirtings, architraves, cupboards, &c., and ½ lb. was applied to the upper surface of the ceilings.

The importance of the ceiling treatment was realized when failure to obtain complete control with repeated applications of 10 per cent. DDT dust in the rooms was followed by successful control when ½ lb. of the dust was applied to the upper surface of the ceilings.

For the control of silverfish infestations in offices, a pyrethrum-DDT spray is effective for treating open filing racks, &c., which are in daily use. This spray treatment is used to complement treatment with 10 per cent. DDT dust, as recommended for houses.

Re-infestation of houses from wood heaps led to a recommendation for the control of silverfish in these places, namely periodic clearing of wood debris and treatment of the lower part of the stacked wood with ¼-½ lb. of 10 per cent. DDT dust.

Successful control of severe infestations of the German cockroach (*Blatella germanica* (L.)) in large kitchens at civilian and service hostels was achieved by the application of 3-5 lb. of 10 per cent. DDT dust to crevices, especially those occurring in the warmer parts of the kitchen, such as around the stove, hot water pipes, boilers, or under sinks.

### 1. Introduction

Womersley (1939) records *Ctenolepisma longicaudata* Esch. as a common pest of houses and libraries in Australia, and Lindsay (1940) records this insect from as far north as Cairns, Queensland, and as far inland as Broken Hill, New South Wales. Notes from Agricultural Journals in New South Wales, Victoria, and South Australia indicate that *C. longicaudata* is a very common household pest in these States.

When large numbers of silverfish were required in 1941 for laboratory experiments at Canberra, approximately 1,000 were obtained from Brisbane. These proved to be *Ctenolepisma urbana*, a species described by Slabaugh in 1940. *C. urbana* has since been identified from Canberra, but *C. longicaudata* appears to be the predominant species in the district.

* An officer of the Division of Economic Entomology.

Silverfish are very common in Canberra. They damage artificial silk and paper of various kinds, particularly those containing starch or sizing, such as wall papers and photographs. They are especially destructive to the flimsy paper used for typing air-mail correspondence. According to Lindsay (loc. cit.) silverfish cannot live on wool or pure silk.

The German cockroach (*Blatella germanica* (L.)) is a very common pest in the kitchens of hostels and in homes equipped with a continuous hot water service. Heavy infestations developed in Service establishments erected in the Canberra district during the war years 1939-45. The Division of Economic Entomology was asked to help deal with these infestations, and it was observed that when a DDT dust was applied to the hiding places of the German cockroach, not only this pest, but silverfish in addition, were effectively controlled.

## 2. Previous Work on Silverfish Control

Several Australian workers have given attention, at various times, to the problem of silverfish control. G. F. Hill, in 1935, initiated the investigations carried out by the Division of Economic Entomology. Lindsay (loc. cit.) and Swan (1941) have published work on the life history, food, damage, and control measures.

Sodium fluoride and fluosilicate dusts are not satisfactory and, until the discovery of DDT, baits and sprays offered the most effective means of control. The Division of Economic Entomology (Anon. 1936, 1939) recommended barium fluosilicate incorporated in a sweetened flour paste, painted onto cards, and placed in cupboards and other places where silverfish abound. The persistent use of the C.S.I.R. bait cards reduced silverfish populations in many houses to a level at which they no longer caused important damage. Both Lindsay (loc. cit) and Swan (loc. cit.) recommended variations of the above bait.

Although barium fluosilicate bait cards have proved efficient in houses, they have been a complete failure in offices where there is a superabundance of attractive alternative food. Many thousands of cards have been distributed in Canberra offices infested with silverfish, but very few have been attacked. To cope with silverfish in Government offices, and in the Parliamentary Library, a high-grade pyrethrum spray was recommended, and a regular programme of treatment, using a spray containing 0·17 per cent. w/v pyrethrins, was initiated, each office being sprayed at approximately six-month intervals. This spray schedule effected a marked reduction in the nuisance, although control was by no means complete. Shortages of staff and materials during the war years caused a partial abandonment of this programme, and silverfish populations steadily increased and were regaining pest proportions when the Divisional investigations were resumed.

In the meantime DDT had become available, and its various uses were being investigated. Davies (1946) and others reported promising results from preliminary tests against silverfish with DDT sprays and dusts containing 5 per cent. DDT.

### 3. Investigations on the Control of Silverfish in Houses

The successful control of silverfish that was achieved by the application of 10 per cent. DDT* in kitchens, carried out with the object of dealing with *Blatella* infestations, has already been mentioned. This led to further tests with this material.

No attempt was made in these tests to compare the efficacy of 10 and 5 per cent. dusts. It was appreciated that silverfish could probably be controlled by the use of a dust containing less than 10 per cent. DDT, but it now well established that a concentration of this order is required for the effective control of cockroaches, and therefore it is obviously desirable that dusts marketed for use against household pests generally should be standardized at the higher strength. Moreover, it is safe to assume that a 10 per cent. dust will remain effective for a longer period than a 5 per cent., thus permitting a longer interval to elapse between retreatments. As the labour involved in a thorough dust treatment far outweighs the cost of the material used, this consideration is of obvious importance.

The first test treatment was carried out in a heavily infested eight-roomed house. A total of 1½ lb. of 10 per cent. dust was blown into the crevices behind skirting boards, architraves, picture rails, &c., and into the spaces behind cupboards and stored lumber. Numbers of silverfish were driven out of their hiding places during the treatment, and several hours later many displayed characteristic symptoms of DDT poisoning. In the days immediately following the treatment, large numbers of dead silverfish were found on the floor of every room treated. A total of 483 were collected during the first two days; an additional 173 were counted in the third and fourth days, but after this the numbers declined, and two weeks after treatment there was an average daily count of only ten dead silverfish. The results of the treatment of this house are shown graphically in Fig. 1(A).

A series of tests was then arranged to determine the degree of control that could be expected if treatment was carried out by householders themselves, after receiving instructions on where and how to apply the dust. Altogether over forty houses were treated. It was hoped to obtain records of the numbers of dead silverfish picked up daily in each room over a period of four weeks after treatment. Most of the co-operating householders, however, ceased keeping records once it was evident that reasonable control had been achieved. The amount of dust used per house varied from 1 to 1½ lb., and the time of application was left to the occupants. From the results obtained it was evident that treatments carried out in daylight were as effective as those undertaken at night.

The records from those houses in which counts were maintained provide a good picture of the effect of the treatment on infestations of varying degrees of intensity. The results obtained are represented in Fig. 1 (B—J). The numbers of dead silverfish counted, and recorded in Fig. 1, do not of course represent the total mortality caused by the dust treatment. Many insects must have died in crevices away from sight, and in several houses large numbers of dead silverfish were discovered behind lumber, &c., when this was moved some weeks after treatment.

* Percentage calculated on p-p' isomer basis.

In most of the houses treated, complete control of silverfish was attained, that is to say no evidence of any survivors was seen after a reasonable interval. In a few houses, however, small numbers of silverfish continued to be in evidence. It was noted that these were confined to the upper part of the building, i.e., the walls, &c., above the level of the picture rails, and the upper floor of two-storied homes. This observation led to an appreciation of the importance of ceiling treatment.

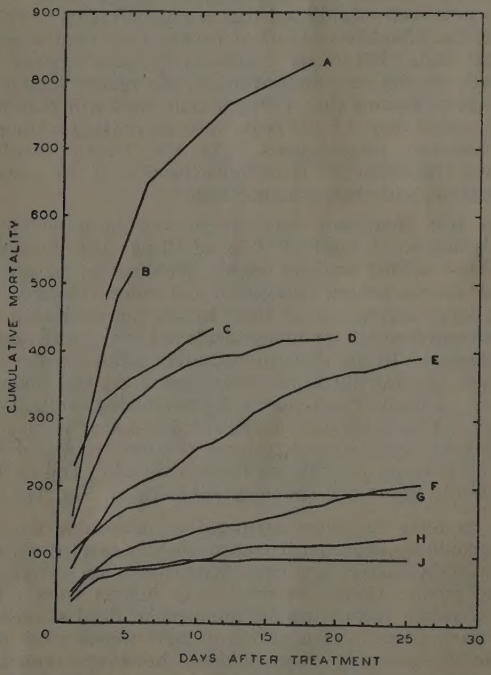


Fig. 1.—Cumulative mortality curves from silverfish-infested houses treated with 10 per cent. DDT dust.

After an interval of approximately three months, the houses in which silverfish were still in evidence were re-treated, with the same technique and the same amount of dust as were used in the original treatments. No marked mortality among the surviving silverfish resulted, and in two of the houses so treated silverfish continued to be seen in the upper parts of certain rooms. By this time it was suspected that the surviving infestation was harboured in the roof cavity. Accordingly, the upper surface of the ceiling of each house was treated, using ½ lb. of dust. This was followed by a sharp and substantial increase in the tally of dead silverfish, and then by the complete disappearance of the insects from the premises. The effect of one of these ceiling treatments is shown in Fig. 2.

### 4. Reinfestation from Wood Heaps

During earlier work connected with the use and distribution of bait cards, it was noted that heavy silverfish infestations in houses were usually associated with wood heaps, the collection of debris at the bottom of which almost invariably harbours a large silverfish population. A check in garages with wood heaps adjoining revealed concentrations of silverfish on the sides nearest the heaps. An analysis of mortality counts from treated houses showed that rooms with fires (kitchens, lounges, laundries) provided the highest tallies; in no house did a bedroom contain the maximum number of silverfish. Daily observations and counts of dead insects carried out in one house over a period of 55 days showed that healthy silverfish appeared after the replenishment of firewood in the kitchen, laundry, and bathroom (which contained a chip heater).

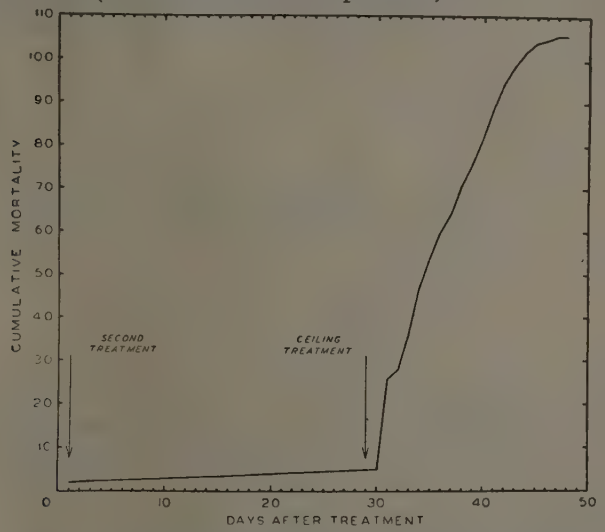


Fig. 2.—Cumulative mortality curve from a house in which the upper surface of the ceiling was treated with ⅛ lb. 10 per cent. DDT dust, after retreatment of the rooms had proved ineffective.

This evidence confirms that obtained by the author from an examination of many wood heaps over the past decade, and leaves little room for doubt that infested firewood provides a continual and important source of replenishment to the silverfish populations in Canberra houses. The author is satisfied that this problem has been completely solved in his own home by (i) clearing the wood heap site of all debris at least once a year, and (ii) blowing ¼–½ lb. of 10 per cent. DDT dust into the bottom half of the heap after restacking the wood.

### 5. Dust Treatment in Houses: Equipment, Technique

For the application of the DDT dust in a manner that ensures its effective penetration into the crevices where silverfish hide, some form of blower is essential. The small insecticidal powder applicators,

consisting of a rubber bulb and nozzle, can be used, but they are not really suitable. More satisfactory is a hand dust gun of the type shown in Fig. 3(A), which was used in the trial treatments described in Section 3. For the treatment of narrow crevices, such as those behind skirting boards and picture rails, with a minimum of mess and waste, a simple modification of the gun is desirable. This consists of a small metal fishtail tube, 2–3 inches long and with a slit opening $\frac{1}{8}$-in. wide and about $\frac{5}{8}$-in across, attached by a few inches of rubber tubing to the outlet of the duster (see Fig. 3). A makeshift fishtail can easily be made by cutting off the requisite length from the extension tube supplied with the duster, and compressing one end to form a slit. If the rubber connection mentioned above is replaced by flexible metal gas tubing the efficiency of the gun is further increased, as the connection is then sufficiently rigid to do away with the necessity of holding the fishtail nozzle with a finger when it is desired to direct the dust stream upwards or downwards.

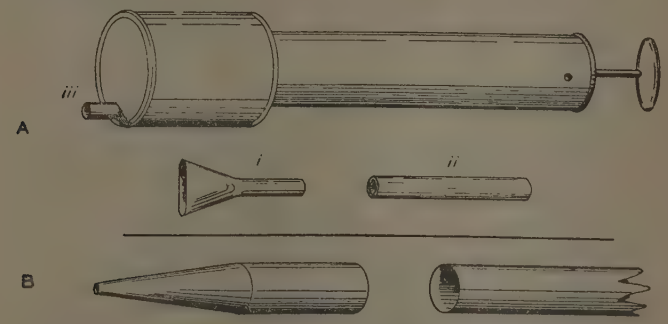


Fig. 3.—A.—Modification of hand dust gun. The metal fishtail outlet (i) is connected by a length of rubber tubing (ii) to the outlet pipe (iii) of the gun.

B.—Modification of discharge tube of knapsack duster showing attachment for reducing width of dust stream.

For large-scale operations a modified knapsack duster is preferable to the small hand gun. The discharge tube of this duster is shown in Fig. 3(B), and is described in the section dealing with the control of the German cockroach.

It must be emphasized that the test treatments described above, which resulted in such satisfactory control of silverfish infestations, were very thoroughly carried out. The object of the operators was to get dust into every crevice likely to harbour the insects. Each room was systematically gone through, and dust blown into the crevices behind skirting boards, architraves, and picture rails, not merely here and there, but at close intervals, and in such a manner that the dust was driven some distance along the crevice from each point of application. Special attention was also given to crevices

around fireplaces, and in built-in cupboards, &c.; and dust was blown into the spaces behind bookcases, wardrobes, and other pieces of massive furniture set close to the walls.

To treat the upper surface of ceilings, it is necessary, of course, to get into the roof cavity via the manhole. In a small house of simple shape it may be possible for an operator to distribute the dust sufficiently well while standing on steps with his head and shoulders through the manhole. Normally, however, it is necessary to go into the roof cavity and to blow the dust about so that it is well distributed on settling.

Examinations of, and reports from, treated houses indicate that a thorough treatment with 10 per cent. DDT dust, using the quantities and carried out in the manner indicated, should maintain a house virtually free from silverfish for a period of twelve months.

Most samples of 10 per cent. DDT dust handled by the Division of Economic Entomology have been practically odourless. Some, however, have had quite a strong odour, and their use in buildings has led to complaints by the occupants. It is desirable to make certain therefore, before treating a dwelling, that the dust to be used is free from any objectionable odour.

When treating rooms in which food is exposed or stored, precautions should be taken to prevent its contamination. Eatables should either be covered or temporarily removed.

### 6. Treatment of Offices

In some offices, and in certain parts of most of them, the use of DDT dust for silverfish control, such as is recommended for houses, is quite practicable. Officers of the Division have given demonstration treatments in one or two large Government buildings in Canberra, with, as far as can be ascertained, very satisfactory results.

In offices where the main infestation of silverfish, and the material that it is desired to protect from damage, is in filing racks, record cabinets, &c., that are in daily use, the application of dust is not desirable. For the control of silverfish in such offices, the use of a spray containing 0·17 per cent. pyrethrins and 4 per cent. DDT in deodorized kerosene was recommended to the Curator of Public Buildings, in the Department of the Interior, and is now in routine use.

The spray is applied with a power spray gun, fitted with a hook which allows the operator to hang the gun on his belt while climbing and moving the ladders required to treat filing racks. After blowing a fine spray into the spaces and crevices, to effect an immediate kill of the insects exposed or disturbed, the operator coats the tops and sides of the pigeon holes, &c., with the spray to leave a residual deposit of DDT. The efficacy of the residual treatment is indicated by reports of the appearance of dead silverfish weeks, and even months, after a building has been treated.

### 7. The Use of 10 per cent. DDT Dust to Control the German Cockroach

The efficacy of DDT against cockroaches is now well established and, as was mentioned in a previous section, the need for a dust containing a concentration of the order of 10 per cent. DDT for the control of the more resistant German cockroach is now recognized, chiefly as a result of accumulated practical experience in the United States of America.

At the time when the Division of Economic Entomology was called on to help deal with heavy infestations of the German cockroach in the kitchens of Service establishments erected in and near Canberra during the war years, information on the properties of DDT was still rather rudimentary. After a 5 per cent. dust had failed, in a preliminary trial, to give the degree of control desired, a 10 per cent. DDT dust was used in several large-scale treatments, with very satisfactory results.

For these treatments a knapsack duster was used, with the discharge tube modified to produce a fine stream of dust at increased pressure. The modification consisted of a conical metal attachment fitted over the end of the discharge tube, and tapered to a small hole of approximately $\frac{1}{4}$-in. diameter (see Fig. 3(B)). The junction between the attachment and the outlet tube was bound with adhesive tape to prevent the escape of dust. Modified in this way, the blower proved extremely effective: it was found that the dust stream could be driven a distance of 8–10 yards when required.

The technique of applying dusts for the control of cockroaches is essentially similar to that employed for silverfish control, i.e., it is blown into the crevices that provide the insects' daytime hiding places. Special attention, however, has to be paid to the crevices around ovens, hot-water containers, and pipes, where *Blatella* tends to congregate.

Between 3 and 5 lb. of dust was used in each of the kitchens treated. Many cockroaches emerged from their hiding places while the treatment was in progress, and within an hour they were distributed over the walls in considerable numbers. For several days after the treatment was applied very large numbers of dead and moribund insects were swept up from the floor. Immobilization apparently took some time, and the erratic movements of the insects affected by the DDT necessitated measures being taken to prevent them getting into food containers.

Discontinued occupation of many of the establishments prevented an assessment of the presistence of the effects of the treatments carried out. One of the kitchens treated with 10 per cent. DDT dust, however, has remained virtually free of cockroaches for a period of over two years.

A trial treatment with hexachlorocyclohexane ("666") was carried out in one kitchen. A dust containing 5 per cent. of the crude material (0·63 per cent. of the gamma isomer) was used. Effective control was obtained, but the odour of the dust was so persistent and objectionable that the use of this material could not be recommended.

## 8. Acknowledgments

The author is indebted to those householders whose tallies of dead silverfish provided data for this paper. He is particularly grateful to Messrs. G. A. McIntyre and K. J. Prowse for their suggestions and enthusiastic collaboration in the treatment of their homes, to Mr. L. Lott for his co-operation in the treatment of Government offices, to Mr. D. G. Venables for assistance in assembling data and for the diagrams and graphs, and to Mr. F. N. Ratcliffe for assistance in preparing the manuscript for publication. Earlier work on silverfish control, during which some of the observations recorded in this paper were made, was carried out under Mr. G. F. Hill. Messrs. F. J. Gay and D. F. Waterhouse, who continued the laboratory studies initiated by Mr. Hill, were frequently consulted during the course of the experiments in practical control. Mr. Waterhouse was in charge of the team from the Division which undertook the treatments of the *Blatella*-infested kitchens.

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# Recent Progress with Pelagic Fishing in Tasmanian Waters

*By M. Blackburn, M.Sc.,* and A. M. Olsen, M.Sc.**

*Summary*

The Tasmanian pelagic fishing experiments, which were begun in 1941, reached a very promising stage in 1947. Two commercial-sized catches of horse mackerel were made by purse-seine under circumstances which suggest that much more can be achieved with larger gear. Lampara net catches of sprats were obtained more regularly and efficiently than before, and this work now has commercial prospects if conducted as an adjunct to other operations. Though limited, these results surpass any previously achieved in work of this kind in Australia.

Reference is made to many past difficulties which now seem to have been overcome. Such work requires the collaboration of skilled local fishermen, whose interest in it is now steadily growing.

## Introduction

For several years it has been a major responsibility of the Council's Division of Fisheries to try to demonstrate commercial methods for the capture of Australian pelagic fish. In spite of the considerable abundance of suitable shoals in many areas at certain times, the work has been marked by very great difficulties. These arose out of certain unsuspected features of the fish occurrences themselves, inexperience with the methods, and latterly shortages of manpower and equipment. Some small successes were obtained at times, e.g. see Flett (1944), but these could not be repeated regularly. It was in 1947 that the experiments first achieved any degree of real success, and the following account is given for the possible guidance of others who will be doing similar work in the near future. It is hoped that the history of the Tasmanian project will indicate that progress can be made where there is perseverance, adaptability, and co-operation between all interested organizations. At present trade conditions are appropriate for pelagic fisheries development in various parts of Australia, especially south-eastern Australia, in a way in which they mostly were not before the war, and there are capable fishermen and merchants who are willing to co-operate in the necessary developmental work. Partly for this reason, pelagic fisheries development in Australia will now probably be much more rapid.

The developments in question were concerned with two species in south-eastern Tasmania, the horse-mackerel (*Trachurus novaezelandiae*) and the sprat (*Clupea bassensis*). The former is known there as "mackerel" and this usage is followed here. Both species have been receiving attention from the Division for several years, and details of the preliminary catching experiments have been given in a previous report (Blackburn, 1943). As was shown in this report, these particular fish and their environment were by 1941 revealed to be more suited to offshore fishing with large surface nets than anything else encountered in the eastern Australian region, and a limited success was achieved in respect of purse-seining for mackerel in 1943, with two catches of which the larger was four tons. Although this

* An officer of the Division of Fisheries.

was very little it represented the best performance with any surface net in Australia to that date, and the only successful one by purse-seine.

## The Mackerel Work, 1944 - 1946

For various reasons, no further advances were made, and even these limited successes could not be repeated in the three seasons following 1943. The optimum season for shoaling mackerel in these waters is from about February through to June. For the 1944 mackerel work, two boats operating different types of nets were used. The State fisheries vessel *Liawenee,* a 67-foot boat of the Danish-seiner class, worked during April, with a kind of purse-lampara net measuring about 330 by 12 fathoms. Mr. H. Watt's 56-foot ketch *Mary,* which had made the catches of the year before, used a purse-seine about 160 by 13 fathoms. This was some 40 fathoms longer than than one previously used, which was too short to encircle shoals regularly. Owing to the extreme shortage of netting in Australia, particularly in the finer mesh sizes, the net was made largely from 2½-inch mesh webbing with the addition of a limited quantity of finer material from the Division.

No success was achieved by either team, in spite of the presence of suitable shoals in adequate numbers. The men on the *Liawenee* found that the great length of their gear enabled them to encircle even fast-moving shoals, but the time required to purse a net with such a high length : depth ratio, without sinking the corks, was so long that the fish would get out. This difficulty had been foreseen, but it was thought it might be overcome by heaving in the wings very quickly by hand before pursing; however, in practice this was beyond a crew of nine men. There was some indication that the net might have worked well for fishing in smooth-bottomed waters within its own depth (as originally intended by its designers), but this did not altogether meet the circumstances of the mackerel problem and the work was not continued. The *Mary* worked much longer and set her gear oftener, but with the same result. The main trouble seemed to reside in the mesh size which allowed most of the fish to escape (one shoal got away completely in this manner after the net had been fully closed and pursed around it), but it also appeared that the net was still not long or deep enough to trap any but the quietest shoals.

After much discussion of these results it was decided that the ordinary purse-seine technique still promised favourably if better gear could be secured. The Council undertook to import a net, and specifications were prepared by those most closely associated with the work. An order was finally placed in the United States for a California-style purse-seine of 2-inch mesh and approximately 200 by 20 fathoms. From about this time onwards the Division of Fisheries initiated overseas orders for small lots of other nets that seemed likely to be useful for future pelagic fishing projects.

The net did not arrive until September 1945, and so nothing much could be done in the mackerel season of that year. Actually the *Mary* carried the old net for two months, but this was not expected to and did not lead to any very useful result. The season was more or less normal as regards fish occurrences.

For the beginning of the 1946 season the new purse-seine was carried by the *Mary,* which, as feared, proved not large or well-powered enough for such big gear, and after a short period it was transferred to the *Liawenee.* It was carried by her for a considerable time, but again there was intense disappointment, this time from a different cause. For the first time in at least six years, the shoals did not appear in their usual numbers, and there were virtually no opportunities for setting the net. One reason for concentrating so much effort on this particular resource had been that it seemed an unusually stable one, the order of abundance of the shoals being practically constant from year to year at the same season, which is not so with most of the other pelagic fish occurrences investigated in eastern Australia (this question has been discussed in detail by Blackburn and Tubb, unpublished). Naturally a non-fluctuating resource is to be preferred for a long-range series of fishing experiments. However, the 1946 season was definitely exceptional for these mackerel, probably not so much because of variation in their abundance in the area as because of a change in their availability at the surface where they might be sought by purse-seine, and it appears that this was mainly due to the very inclement weather at that time. Thus this season also passed without any success being achieved.

Unfortunately, the unsuccessful results caused a waning of interest in mackerel by the trade. Previously, Tasmanian fish canners and curers had been rather short of fish, but from about 1944 onwards they were able to obtain large supplies of barracouta, and mostly had more fish than they could comfortably handle. This turn in events was not really unexpected, since Tasmanian fishermen have always been more used to hook-fishing than netting in any form. Indeed one of the main troubles with the purse-seine work was the constant difficulty of obtaining men who could efficiently handle nets. It was hoped to obtain a skilled purse-seine operator from abroad, but in the outcome nothing was done.

## The Mackerel Work in 1947

The situation was eventually relieved because of developments in New South Wales, where conditions were very different from those in Tasmania. Here, the immediate post-war period found fishermen and processors with not enough fish, instead of too many as in Tasmania. At the Narooma cannery there had been a shortage for years. On the fishermen's side, the abundance of "trawl" fish had not greatly improved from their war-time "resting" as was hoped, and indeed what was formerly the main species, tiger flathead, became scarcer than before. This affected the small-boat operators particularly, and some of them began to consider undertaking other kinds of fishing. Unlike the Tasmanians, many of them had had considerable net-fishing experience, including with large beach-seines for Australian salmon and other species, and it was natural for some to think about pelagic net fishing for the shoaling species of their own waters. The Division of Fisheries was in fact approached by two or three groups of fishermen for loans of gear for this work, which were all met as far as possible, but the details of only one such arrangement, the only successful one to date, are relevant here.

The vessel was the *Eden Star,* a boat of the Danish-seiner class (Fig. 1). She is 61 feet long with 18 feet beam and 9 feet draught, and has 102 h.p. with a speed of about 9 knots. The owner, Mr. W. Warn, borrowed the mackerel purse-seine from the Division in January, 1947, and spent 10 days in Tasmanian waters. An aerial reconnaissance located one extensive body of fish, but a change of weather prevented advantage being taken of this. Tests were then carried out near Eden (N.S.W.) for nearly two months.

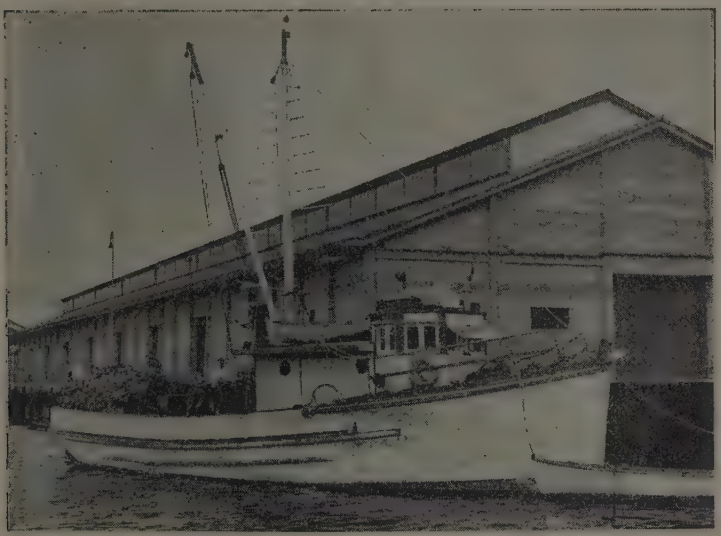

Fig. 1.—The *Eden Star* with purse-seine net. (Photo., Hobart "*Mercury.*")

The *Eden Star* and her crew encountered here all the main difficulties that the Division had met with in its own work on the mainland coasts over several years, namely, much unsuitable weather and wildness of the shoals offshore, inadequate depth in which to net the quieter inshore occurrences with this gear, and, at the last, the disappearance of most of the fish. When it was found that the purse-seine was too deep for shooting in Twofold Bay where many of the best occurrences were, the men built a purse-lampara or ring-net about 250 fathoms long, from material owned partly by the Division. With this they made one catch of 2 tons of bonito (*Sarda australis,* the "horse-mackerel" of New South Wales fishermen), which was in its way quite notable as being the first haul of any tuna species by surface seine in Australia. However, these fish took off before anything more could be done with them. Subsequently this net was dismantled to yield materials for lengthening the purse-seine by over 50 fathoms, after it was found that the latter would not encircle some of the fast-moving offshore shoals, but by the time these alterations were made the major fish concentrations had disappeared altogether. This made a return to Tasmania appropriate, and the vessel arrived there in the last days of March.

Mackerel were first observed a few days later in Monroe Bight. A very large shoal was encircled but it escaped by tearing away nearly all of the added lighter netting. Seals added to the damage, and considerable repairs were necessary. During the following 9 days' cruise the weather was somewhat unsuitable, and only one good occurrence of fish was encountered. This was in Fortescue Bay, in the vicinity of the previous attempt, and there was again interference by seals, which caused the selected shoal to submerge as the net was about to be set. Darkness fell within a few minutes (these mackerel often shoal at their best in the last hour of daylight) and there was no chance to manœuvre for a second attempt. The fish were not found here thereafter, or elsewhere, and an aerial survey of the whole south-eastern Tasmanian area also failed to locate any significant occurrences at this time. It might be observed that those responsible for the earlier tests had had little regard for the east coasts of the Forestier and Tasman Peninsulas (including the localities mentioned above) for this work, in spite of frequent mackerel occurrences at times. This was because of seals which are particularly numerous there, and also the very strong currents which tend to confine any surface netting activity to the one or two available bays.

The next cruise was in the Maria Island area, and on April 23 a suitable shoal was located and followed for almost 2 hours before a favourable opportunity for shooting the net occurred, at 4 p.m. This shot was very successful and yielded about 15 tons of mackerel averaging 2½ lb. The locality was off Oakhampton Bay in about 22 fathoms, and the sea was calm and general conditions ideal. Six days later the second catch, of about 16 tons, was made near Cape Bernier, at about the same hour and under similar weather conditions. In the early afternoon several shoals were found close inshore, but the vessel managed to work one of the larger ones into the deeper water where the purse-seine could be used. During the pursing some more of the lighter netting, which had again been added to increase the length of the net, tore under the weight of fish. In consequence a large part of the catch was lost, leaving only the 16 tons which were actually got aboard. These fish averaged about 2 lb.

The fourth cruise of the series commenced on May 5, after repairs to the net had been effected. The *Eden Star* returned to the Maria Island area and had no trouble in locating fish, which were also found here in the course of an aerial reconnaissance during the same period. Five sets of the net were made but were all unsuccessful. What had been suspected on some earlier occasions was now established, that the gear as imported was too short to encircle the most active shoals, at least without frightening them so much that they would submerge before the net was pursed. It was found in earlier years that the shoals often become livelier, and do not stop up so well at the surface, towards the end of the season. However, the successes of the *Eden Star's* two April hauls were probably also due to the lengthening of the net, whereas there was no material left for this on the fourth cruise. Finally the net was measured and found to be only 170 fathoms long instead of the 200 specified. The Division then made available some old netting it had in Hobart, and the length was again increased to about 200 fathoms. A fifth cruise was made for a few

days at the end of May near Maria Island, but the shoals found were quick and erratic in their appearances and the two shots made were unsuccessful. The *Eden Star* carried six men throughout her work.

### Comment on the Mackerel Work

The two purse-seine catches made by the *Eden Star* represented the first truly commercial-scale hauls of any pelagic fish by any surface net anywhere in Australian waters. Had this performance been repeated even once or twice more the whole question of the suitability of the method in this particular case would have been at an end, but what has actually been achieved is in itself extremely promising. One might be more doubtful if there was no reasonable explanation for the seven subsequent failures, or if it was not practically possible to correct what was at fault on these occasions, but this is not so. It is quite plain that a net 170 fathoms long is too short to take the fish regularly (which incidentally indicates that the three-man crew of the *Mary* did remarkably well to take the fish they did in 1943 with 120 fathoms), but that a longer one is suitable for this purpose. As shown above, it was always thought after 1944 that 200 fathoms would be necessary, but the crew of the *Eden Star* now believe that as much as 250 fathoms is required to cope with all eventualities. As was emphasized in the published 1943 report, one has to consider the depth of water also in connection with the lengthening of the net, because if the length : depth ratio very greatly exceeds 10:1 the corkline will sink and release the fish in the pursing process, unless this is so slow as to run the risk of loss of fish by their submergence. However, although mackerel may shoal in 10 fathoms of water or less, the experience of many seasons' work now indicates that schools also occur fairly often in waters of between 20 and 25 fathoms, though much less commonly further out. Therefore (bearing in mind also that purse-seining can be carried out in shallow water if the bottom is smooth) a net of maximum length 250 fathoms and minimum depth 20 fathoms would probably meet all the requirements of this work. The maximum ratio in this case, $12\frac{1}{2}$ : 1, is high, but it is found in some commercial Californian nets (see Fry, 1931, p. 19). At the time of writing the Division of Fisheries is assisting Mr. Warn to enlarge the present gear on these lines, for further work in New South Wales and Tasmania.

The question of what actually constitutes economic fishing depends on operating costs and available prices for the fish, which may both vary considerably. However, it can be said, for example, that an average catch of 15 tons per fortnight, i.e., much less than obtained by the *Eden Star* in its period of success, would at present prices constitute a very good return for a boat and crew such as was operating in this case. Even if prices fell, as they might if such quantities were regularly landed, there would still be some margin. However, there is reason to suppose that, with proper gear as suggested above, the rate of catch would be higher than this. The experience of the *Eden Star's* second haul suggests that quantities well over 15 tons could probably be taken in a single catch at times, and, furthermore, it is certain that opportunities for setting the net, on large shoals under good conditions, would occur oftener than

fortnightly. In the unpublished report by Blackburn and Tubb mentioned above, the records of Tasmanian mackerel shoals of several seasons were very fully analysed, and it was shown that sizeable concentrations suitable for purse-seining were liable to be found on an average of 1 in every 5½ days, over the 5-month season February to June, in nearly every year. Allowing for some shots being failures, and for occasional bad seasons such as 1946, it appears nevertheless that the work might prove very profitable. At any rate it has been shown that the method is quite feasible and will yield large catches, and, although a demonstration of continuous catching has yet to be made, there is no longer much doubt, in the mind of anyone associated with the work, that it will eventually prove a sustained success in Tasmanian waters. Tests under proper conditions will shortly be carried out in New South Wales waters. In both States there is now a considerable demand for good quality canning fish.

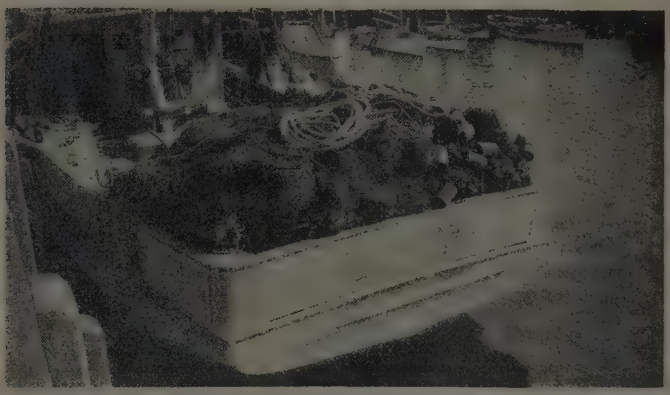

Fig. 2.—Stern of the *Eden Star* with purse-seine ready for use. Note rings over port side, with purse-line running through from large coil on deck. (Photo., A. M. Olsen.)

Fig. 2 shows the stern of the *Eden Star* with the purse-seine ready for use. It will be seen that there is no turntable and that the winch is of the ordinary " Danish-seine " type. An interesting point is that the purse-rings hang together over the side and the purse-line runs through them from a large coil on the deck. This is not, or at any rate was not formerly, the Californian practice with purse-seining, although something very similar is done in respect of ring-net work (see Fry, 1931, pp. 40–2). Thus the purse-line and purse-rings of such nets that were carried on the Division's vessel *Warreen,* from 1938 to 1942, were always piled in with the leadline following Californian practice, and this gave constant trouble with the kinking of the purse-line, so that there were many times when pursing could not be completed. When Mr. T. Challenger and the senior writer commenced their operations in 1942 the other method was tried and proved an immediate success, so that it has been used by all crews since in this Tasmanian work.

The localities on the south-east Tasmanian coast that have been found particularly good for mackerel shoals, leaving aside some that do not lend themselves very well to purse-seining as noted above, are from north to south Cape Lodi, Wineglass Bay, Schouten Passage, Oakhampton Bay, Darlington, Reidle or Halfmoon Bay, Cape Bernier ("Hellfire Bluff"), Green Island, Fortescue Bay, Wedge Island, and Adventure Bay. The more landlocked waters, such as the D'Entrecasteaux Channel, and Frederick Henry, Norfolk and Blackman's Bays, are poor areas. Mackerel also occur north of Cape Lodi but seem less conspicuous there in shoals.

## The Sprat Work

Concurrently with the mackerel effort, the Division and its collaborators have continued to devote some attention to the question of fishing Tasmanian sprats. As a result of the 1947 trials in particular, this project can now be regarded as satisfactorily established from the trade side, although no very high level of output can reasonably be looked for here. The fish are true sprats which are very closely related to those of that name that support a sizeable fishery in the North Sea and the Baltic, and which before the war were available in Australia as canned "sardines" or "sild" from Norway (see Blackburn, 1941, p. 52). Apart from a probably erroneous record from South Australia the species has not been reported outside Tasmanian waters. It has been found as far north and west as Flinders Island and the Tamar River, but in the experience of the Division's officers it is most abundant in Storm Bay and adjacent waters. Actually, although shoals have been reliably reported elsewhere, the only ones seen in the course of the organized survey work have been in the southern waters of the D'Entrecasteaux Channel. The limits of the season there are not precisely known, but probably the surface shoals are most numerous from about March to June. At this season, it has been found that good concentrations are liable to be found on about one day in nine on an average, although there is some slight annual fluctuation (Blackburn and Tubb, unpublished).

These sprat shoals were first noticed by the Division's workers in 1940, when the *Warreen* attempted to catch them by lampara net. These attempts failed, but in the following year there were a few significant catches, including one of about 2½ tons. A portion of this particular haul on the Hobart wharfs is shown in Fig. 3. The main interest in the species up to then had been in their possible utility for live bait for tuna, but it was found that the fish could not be held alive for this purpose after netting, because of excessive loss of scales (see Flett, 1944). However, it was then considered that they might serve for canning, and when the special co-operative efforts with the Tasmanian Fisheries Division began in 1942 these fish received more attention than mackerel for a time. Further lampara work in that year resulted in a few more hauls of significant size, and it was decided to attempt to catch them by purse-seine in 1943. As shown elsewhere (Blackburn, 1943) these trials did not succeed, partly because of faults in the net but partly also because of relative scarcity of suitable shoals. The main effort was immediately turned to mackerel and proved more successful with that

fish, with the result that the mackerel work has since always been regarded as potentially much more important. The 1943 work also emphasized the localized distribution of the sprat and the very moderate extent to which it occurred in sizeable surface shoals, and it was not long afterwards that it ceased to be regarded as likely to give rise to a substantial independent fishery, by any of those associated with the tests.

Fig. 3.—Portion of catch of sprats made by the *Warreen*. (Photo., J. A. Tubb.)

However, the matter was not lost sight of in the following years. It had at least been established that the fish could be caught with some regularity by lampara net, even though the catches were not large and the opportunities for making them not very frequent. Some of those who had participated in the experiments realized that sprat fishing might at least be profitable if conducted as an adjunct to other fishing operations (such as for barracouta and scallops, which are taken in the south Channel waters at the same season), especially if the fish could be sold for curing, thus commanding a higher price than would be economic for canneries. Practically nothing was done in 1944, but in 1945 and 1946 private operators conducted some more tests with the lampara and other gear provided

by the Division. The catches obtained were small, averaging only a few hundredweight each, but there were nearly always some fish taken. The lampara crews of four men were smaller than at any time before, but this number was still uneconomically large for what was visualized as an essentially part-time occupation for small boats.

In the end it was the general opinion that the lampara was the appropriate gear, since it was small and light and could be stowed away when not required, and brought out, used, and put back without much trouble when sprat shoals were encountered. What seemed to be required was a special lampara with relatively short wings, which would not need so much manpower to haul aboard before the fish could escape. Fortunately the Division had previously placed an order for some such nets in California, and when these arrived in 1946 one was allocated to Mr. T. Sward for use in the following sprat season on his vessel *Valetta*. These nets were about 150 fathoms long, whereas those used previously had been about 200 fathoms. The sprats had for years been remarked as quieter in the shoaling state than any other closely investigated Australian pelagic species, so that the question of length of net to encircle them was not so important.

This net was carried for about seven weeks in March and April, 1947. The area of operations was again the south part of the Channel. It is not clear how many days were actually devoted to searching for shoals, but there were only three on which they were found in good quantities. However, on each of these there were three hauls of the net around sprats, the total daily captures being respectively 2,069, 2,447, and 1,833 lb. There were two negative sets and the other individual catches ranged from about 300 to 1,833 lb. These were of much the same order as obtained previously, but the important points are, firstly, the regularity with which fish were obtained, and, secondly, the small number of men in the crew. This was three, except for one haul for which only two were available, but which, nevertheless, yielded about 750 lb. The operators consider that these results indicate real, if limited, possibilities with sprats for commerce. The writers are informed, by representatives of a leading food processing firm which is using these fish for paste manufacture, that they are particularly suitable for that purpose because of their very fine flavour. This is said to surpass that of the real anchovies and pilchards of Australian origin that are being used for this process by the same company. There are also other possibilities on the marketing side, and with a satisfactory fishing technique available the question of developing the sprat resource can be left to the enterprise of the fishermen and processors.

## Acknowledgments

The successful results obtained in 1947 were only made possible by the collaboration of the Tasmanian Fisheries Division, and of various private operators, with the Council's Division over a number of years. Mention has already been made of the work of Messrs. W. Warn, H. Watt, and T. Sward, and it is also desired to thank all the members of the crews of their vessels. The work on the *Liawenee* was carried out by Captain H. Johnston, Mr. A. Burnett, and also

Mr. W. Warn, who was mate for a period in 1944. Dr. H. Thompson was in the last instance responsible for what was done by the Council's Division of Fisheries, and he was especially concerned with the organizing of the successful 1947 work. Mr. S. Fowler was of considerable assistance on the aerial reconnaissance side in various years, the junior author also participating in this in 1947. Mr. J. A. Tubb gave much useful advice and encouragement at all times. and Mr. W. S. Fairbridge supervised some of the boat work that was done from 1944 to 1946. Probably no one did more throughout than Mr. T. J. Challenger, Tasmanian Inspector of Fisheries, but for whose practical fisheries capacity the work would certainly not have started under the difficult conditions that existed during the war, and whose enthusiasm and patience were very largely responsible for keeping going at times when the prospects seemed almost hopeless.

In conclusion, it is desired to thank the proprietors of the *Mercury* newspaper of Hobart for permission to reproduce the photograph of the *Eden Star*.

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## Addendum

Since the above was written, the *Eden Star* has made two catches of 18–20 tons of the same "mackerel" in New South Wales waters (October and November 1947). This followed the lengthening of the purse-seine to 235 fathoms.

# Laboratory Methods for Testing the Resistance of Textiles to Attack by Fungi

*By G. C. Wade, M.Agr.Sc.**

*Summary*

The pure culture tests used for testing mould resistance of textiles are discussed. *Memnoniella echinata* is used for testing resistance to loss of tensile strength, and *Aspergillus niger* for testing resistance to loss of waterproofness due to micro-organisms.

Test samples are sterilized by exposure to methyl alcohol, which is removed by evacuation in a desiccator or vacuum oven. Samples are then rested on mineral salts and agar medium, inoculated, and incubated for 14 days at 30°C.

Soil burial tests are also described. Greatest loss of strength occurred at 80 per cent. of the water-holding capacity, but for routine tests a moisture content of 65–70 per cent. was used. The relative merits of the two types of methods are discussed.

## 1. Introduction

With the outbreak of war in the Pacific, it became obvious that Australian troops would be required to fight in tropical areas, and that materials of an organic nature, including cellulosic fabrics, would be liable to deterioration through micro-organisms under those conditions.

It was therefore necessary to develop protective treatments, and rapid laboratory methods of testing such treatments were investigated as part of this programme. Two main classes of test methods, namely, pure culture tests and soil burial tests, had been used previously in overseas work and both these methods were studied here, in collaboration with the General Chemistry Section of the Munitions Supply Laboratories, Maribyrnong, Victoria.

## 2. Pure Culture Tests

The principle of these methods is to inoculate the fabric under test with a pure culture of an organism known to cause deterioration of untreated fabric, under conditions favourable to the organism, and after inoculation to determine the effect of the organism on the treated fabric or, in some cases, note the amount of the growth of the organism.

Thom *et al.* (1934) developed a method in which the fabric, after sterilization by autoclaving, was rested on a sterile medium of mineral salts and agar and inoculated by a pipette with a spore suspension of *Chaetomium globosum.* After incubation at 28°–30° C. for 14 days, the tensile strength of the fabric was determined. Subsequent investigators (Furry *et al.*, 1941; Greathouse *et al.*, 1942; Rogers *et al.*, 1940) have changed details of the method, but it has formed the basis of subsequent pure culture tests.

Following work first conducted by Dr. H. L. Jensen in collaboration with the Munition Supply Laboratories, it was found that a number of surface moulds are also of importance on tentage since they reduce waterproofness of the fabric, and test methods have been developed in the course of this work to test efficiency of treatments against these fungi, as well as against cellulose-digesting forms.

* Now an officer of the Tasmanian Department of Agriculture; the work described was carried out while the author was on the staff of the Victorian Department of Agriculture and a member of the Mycological Panel of the Scientific Liaison Bureau.

(i) *Testing Resistance to Attack by Fungi Which Reduce Tensile Strength*

The method of Thom *et al.* (1934) was used in the early work, except that *Stachybotrys atra* was used as the test organism and the inoculation was conducted with an atomizer instead of a pipette. *Stachybotrys atra* has also been used by New Zealand workers (Brien and Dingley, 1946). Cultures of the strain of *Chaetomium globosum* used in America were not available in Australia at the time, and *S. atra* was a more powerful cellulose digestor than any of the *Chaetomium* species then tested. *Memnoniella echinata* subsequently replaced *S. atra* in our tests since it was more common on deteriorated cellulosic materials returned from the service areas, and had similar activity as a cellulose-digesting organism. Greathouse *et al.* (1942) used *Metarrhizium glutinosum* in their work.

FIG. 1.—Showing refrigerator box containing mineral salts and agar medium, and strip of untreated duck which is held in place by single cotton thread.

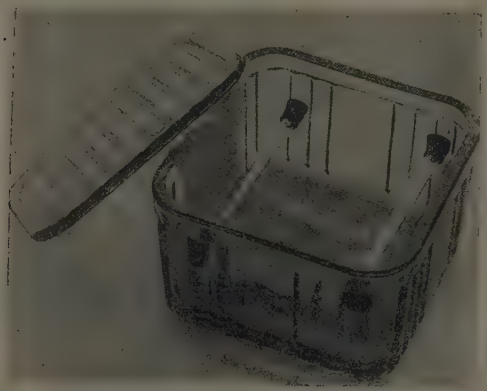

FIG. 2.—As Fig. 1 after cutting cotton thread and pressing duck down on to agar.

Inoculation with a mixture of fungi was not used as it was demonstrated that many of the fungi concerned were antagonistic to one another. In one experiment to check this, untreated cotton duck was inoculated with *Memnoniella echinata, Stachybotrys atra, Chaetomium* sp., and with combinations of the fungi. It was found that if *M. echinata* was present in a mixed spore suspension it became dominant and other fungi were excluded. If duck was inoculated with a mixture of *Chaetomium* and *Stachybotrys* both fungi grew in well-defined areas and did not invade areas already attacked by the other organism. Tensile strength determinations showed that strength of duck inoculated with a mixture of *M. echinata* and *Chaetomium,* or with a mixture of *M. echinata, S. atra,* and *Chaetomium,* was significantly greater, after incubation, than of duck inoculated with *M. echinata* alone.

In order to determine whether the antagonism was due to toxic materials produced by the fungi, an experiment was conducted in which *Aspergillus niger, Chaetomium* sp., *Penicillium luteum, M. echinata* and *S. atra* were grown on Czapek's solution for 14 days. The cultures were then filtered through a Seitz filter and added to Czapek's solution, a similar volume of distilled water being added to another series as a control. Flasks containing each filtrate were inoculated with *A. niger, P. luteum* and *M. echinata.* After eight days' inoculation, the fungal mats were filtered off, dried, and weighed. It was found that *Stachybotrys atra* produces a toxic principle which inhibits the growth of *Aspergillus niger* and *Memnoniella echinata,* and *P. luteum,* a principle which inhibits growth of *A. niger.* Thom *et al.* (1934) and Barker *et al.* (1943) have also found the use of mixed inoculations unsatisfactory.

Refrigerator boxes of the type shown in Figs. 1 and 2 were used. After preparation, the mineral salts medium was distributed to the boxes to give a depth of about ¼ in. in each and two glass rods with pieces of rubber tubing on each end, to prevent slipping of the rods, were placed across the box to hold the ends of strips off the agar (Fig. 2). In preliminary work on the influence of the medium, etc., two strips of untreated fabric each 11 in. by 2⅛ in. were folded over the rods and held in place by a single stitch of cotton (Fig. 1) and the whole sterilized by autoclaving for 30 minutes at 18 lb. pressure. After autoclaving the thread was cut and the strips pressed down in contact with the agar (Fig. 2). In tests of treated fabric, the boxes containing media were autoclaved and the fabric separately sterilized by methyl alcohol, as described later.

The work was conducted using Thom's (Thom *et al.,* 1934) medium of the following formula (Medium A):—

| | |
|---|---|
| Sodium nitrate | 3·0 g. |
| Potassium phosphate ($K_2HPO_4$) | 1·0 g. |
| Potassium chloride | 0·25 g. |
| Magnesium sulphate | 0·25 g. |
| Agar | 10 g. |
| Water | 1,000 ml. |

This medium was compared with that of Greathouse *et al.* (1942) (Medium B).

| | |
|---|---|
| Potassium phosphate ($K_2HPO_4$) | 1·394 g. |
| Magnesium phosphate | 0·740 g. |
| Ammonium nitrate | 1·001 g. |
| Calcium carbonate | 0·005 g. |
| Sodium chloride | 0·005 g. |
| Iron, zinc, manganese as sulphates | 0·001 g. |
| Agar | 10 g. |
| Water | 1,000 ml. |

It was also compared with a medium of distilled water and agar. Mercerized cotton of a breaking strain of 80 lb. per inch width was used for the tests, which were conducted as described above. *Stachybotrys atra* was used as test organism and the tests were incubated for seven days at 30°C. All the tensile strength determinations described in this work were made at the Munition Supply Laboratories, Maribyrnong, using a Goodbrand tester. Six replicates were used. The results are shown in Table 1.

TABLE 1.—EFFECT OF COMPOSITION OF THE MEDIUM ON THE DETERIORATION CAUSED BY *S. atra*

| Medium | Mean Tensile Strength Per Inch Width | pH of Medium* |
|---|---|---|
| Agar-distilled water | 29 | 6·0 |
| Medium A | 3 | 7·5 |
| Medium B | 5 | 6·4 |

* Original pH 7·0.

The analysis of variance as described by Snedecor (1940) was applied to the results.

Difference for significance at 5 per cent. level = 3 lb.
Difference for significance at 1 per cent. level = 5 lb.

This test demonstrated the accelerating effect of a mineral salts medium. There was no significant difference between the results with the two mineral salts media and, since much information had already been obtained with medium A, its use was continued.

To determine the influence of the quality of agar on the test, medium A was prepared using two different samples of powdered Japanese agar, a sample of shredded Japanese agar, and agar of Australian manufacture. The test was then conducted in the usual way, using twelve replicates of mercerized cotton of initial breaking strain of 80 lb. per inch width. They were inoculated with *S. atra* and incubated for seven days at 30°C. The results are shown in Table 2. All the samples of Japanese agar proved equally effective, but the Australian

agar was unsatisfactory, because it gave an inferior gel and the variability of the results as shown by the standard deviation was considerably greater than with the other agars.

TABLE 2

| Agar Used | Tensile Strength | Standard Deviations |
|---|---|---|
| Powdered Japanese agar A .. .. .. | 12·7 | 3·2 |
| Powdered Japanese agar B .. .. .. | 9·6 | 2·2 |
| Shredded Japanese agar .. .. .. | 13·6 | 2·6 |
| Australian agar .. .. .. .. | 19·5 | 13·5 |

Difference for significance at 1 per cent. probability level = 7·2 lb.
Difference for significance at 5 per cent. probability level = 5·4 lb.

Agar was in short supply during the war and Greathouse *et al.* (1942) suggested using a solution of mineral salts with a wick of glass fabric to support the test material. Glass fabric was not available in Australia, but tests were conducted using glass tape wound on a broad U-shaped glass rod, and with washed sand, watered with Thom's mineral salts solution. The strips lost less strength on sand than on agar. The loss of strength on the glass tape frame was not significantly different to the loss on agar, but the results were more uniform. However, the method was not adopted as it was found that the frames could not be cleaned adequately for re-use, and the labour of preparing them was prohibitive for routine tests.

To determine the relative efficiency of inoculation with a pipette and an atomizer, mercerized cotton was laid on medium A in refrigerator boxes in the usual way, and twelve strips inoculated by a pipette and another twelve by a de Vilbis atomizer, using a spore suspension of *Stachybotrys atra* containing 670,000 spores per cc. After incubation for seven days at 30°C., the tensile strengths were determined, and it was found there was no significant difference between the results obtain by the two methods.

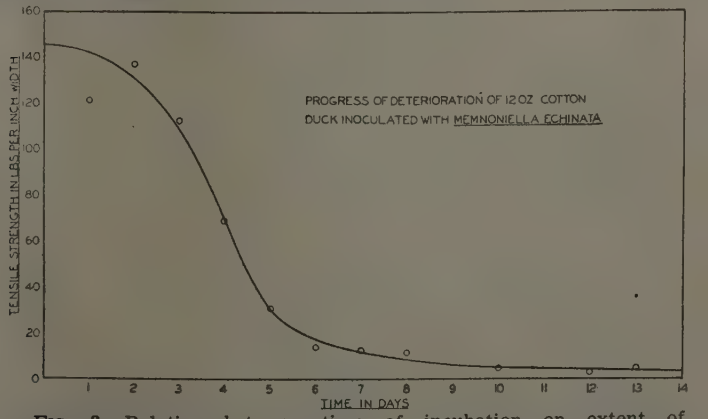


FIG. 3.—Relation between time of incubation on extent of deterioration of 12-oz. cotton duck inoculated with *Memnoniella echinata*.

To determine the effect of concentration of the spore suspension, mercerized cotton strips were inoculated with suspensions of *S. atra* containing 670,000, 380,000, and 120,000 spores per cc. It was found that within these limits the concentration of the suspension had no influence on the results of the test.

To determine the effect of time of incubation on loss of strength of cotton duck inoculated with *M. echinata* and *S. atra,* untreated duck was rested on medium A and four strips removed after each day of incubation and the tensile strengths obtained. The results for *M. echinata* are shown graphically in Fig. 3. With both organisms the loss of strength had reached a maximum in fourteen days and this was adopted as the time of incubation for routine tests.

Tests with treated materials were carried out on the material as received, and after washing in a water spray for seven days (three and a half days each side). It was considered desirable that the leaching should be as severe as possible; the seven-day period was the maximum that was practicable for a routine test. The variation in temperature of the water spray was unfortunately high (17° ± 5°C.), but there is no evidence that this variation is of great significance.

The volume of work necessitated a restriction in the number of test pieces, and experimental work suggested that sufficient data for practical purposes could be obtained from the inoculation of three strips in each test.

It was not always possible to determine the tensile strength of strips immediately after incubation, and they were therefore sterilized by immersion in methylated spirits.

(ii) *Resistance to Attack by Fungi that Reduce Waterproofness*

Work by Dr. H. L. Jensen (1946) in collaboration with the Munitions Supply Laboratories showed that certain Aspergilli and Penicillia were able to attack copper soap-treated fabrics and cause loss of waterproofness, and reports from New Guinea indicated that loss of waterproofness of untreated tentage due to attack by similar fungi was a serious problem. Therefore, in addition to testing for resistance to cellulose-digesting organisms, it became standard practice to test also for resistance to waterproofness-destroying fungi.

Other workers, e.g. Marsh *et al.* (1944), have tested the resistance of treated fabrics to species of *Penicillium* and *Aspergillus,* but have relied on noting the amount of growth, and do not refer to the effect of the organisms on waterproofness. The work conducted here has shown that the determination of the effect of attack of the organism on the fabric gives much more reliable results than noting the surface growth.

*Aspergillus niger* was used as test organism since it was commonly found on both treated and untreated fabrics and caused serious loss of waterproofness. Four circles, 4 inches in diameter, were sterilized with methyl alcohol vapour, and then pressed down on to medium A in petri dishes. After inoculation they were incubated for fourteen days at 30°C., and the waterproofness determined at Munition Supply Laboratories, Maribyrnong, using apparatus developed there, which measured the head of water at which the fabric first showed leakage. In some of the early work, the circles were sterilized with methylated

spirits after incubation, but it was found that this practice led to unreliable results, as impurities in the liquid reduced the waterproofness of the fabric. Also, elimination of the use of methylated spirits obviated any possibility of redistribution of water-repellent substances. In practice, therefore, the test samples were dried out after incubation, and the waterproofness determined as soon as possible.

The amount of macroscopically visible mould growth was also noted, but it was found that there was little correlation between it and the loss of waterproofness.

(iii) *Sterilization Technique*

The use of a sterilization treatment in the testing procedure is necessary to avoid the growth of organisms differing in activity from the test organism and possibly antagonistic towards it.

In overseas work, sterilization by autoclaving has been adopted generally. It is obvious that autoclaving is unsatisfactory when dealing with fungicides that have a high solubility in water or are volatile, and it became evident that autoclaving may also alter the distribution of many non-volatile fungicides that have a relatively low melting point, e.g. copper soaps. Autoclaving can thus only be safely used with a few materials, such as those treated by the cuprammonium process.

It was therefore necessary to examine other methods of sterilization. Schweizer (1931) developed a method of sterilizing culture media, in the cold, by use of volatile fungicides. He listed various volatile fungicides that were effective and described suitable apparatus for sterilization. Very much earlier Krais (1919) used chloroform vapour to sterilize nettle stems in retting experiments. Experiments were therefore conducted to develop a method of using volatile fungicides for sterilization in textile testing. Methyl alcohol was included in the tests as Dr. S. D. Rubbo, Professor of Bacteriology, University of Melbourne, was using the vapour of this material for sterilization of optical instruments.

In the first experiment, 2-in. square pieces of 18-oz. cotton duck were inoculated with a spore suspension of *S. atra.* Four pieces of inoculated duck were immediately placed on the mineral salts and agar medium previously described. Four pieces were placed in a sealed jar containing a layer of methyl alcohol, four in a jar containing xylol, and four in a jar containing chloroform. After exposure to the vapour for three hours at room temperature, the pieces of duck were removed with sterile instruments and placed on mineral salts and agar medium. All samples were then incubated at 30°C. for seven days, when they were examined for growth of the organism. Vigorous growth developed from the unexposed pieces and the pieces exposed to xylol. Methyl alcohol and chloroform gave complete sterilization.

Chloroform was unsatisfactory because of its softening effect on some finishes. The vapours of both chloroform and methyl alcohol appeared to be absorbed by the fabric. Because of its lower solvent properties, methyl alcohol was preferred and it was considered that the amount absorbed was insufficient to affect substantially the distribution of any fungicide or water-repellent substance. Further experiments were conducted at various temperatures to determine the

minimum time required for sterilization by methyl alcohol of duck in which *S. atra* had commenced growth. In this series of tests, 18-oz. untreated cotton duck was inoculated with *Stachybotrys atra* and incubated for 48 hours at 30°C. to enable the fungus to germinate and penetrate the duck. The duck was then exposed above methyl alcohol at 20°, 30°, 40°, and 50°C., and pieces removed at hourly intervals and placed on mineral salts and agar medium and incubated. Under these conditions, sterilization took over 6 hours at 20°, 6 hours at 30°, and was effective in 1 hour at 40° and 50°C.

It seemed possible that sterilization would be less effective with fabric treated with chemicals, such as copper soaps, which would hinder penetration of the volatile fungicides. A test was therefore carried out in which 12-oz. cotton duck, treated with copper soap, was inoculated with *Aspergillus niger*. It was then incubated in a humid atmosphere for 48 hours. Pieces of the duck were then exposed to methyl alcohol and chloroform vapour respectively at room temperatures and at 40°C. and the minimum time for sterilization determined. Methyl alcohol was effective in three hours at room temperature and in one hour at 40°C. Chloroform was effective in three hours at both temperatures.

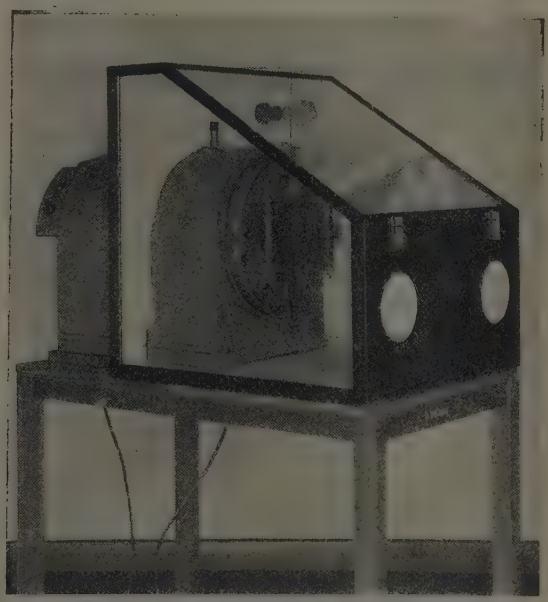

FIG. 4.—Transfer chamber with vacuum oven in position.

Strips of untreated duck retained sufficient methyl alcohol after exposure to inhibit growth of *Stachybotrys atra*. It was found that the methyl alcohol could be completely removed by transferring the fabric, after exposure, to a sterile desiccator, which was placed in an oven at 40°C. and evacuated for one hour.

The time of exposure to methyl alcohol adopted for routine tests was a minimum of four hours at 40°C. or a minimum of twelve hours at room temperature. The transfer of fabrics from the vessel containing methyl alcohol to the sterile desiccator, and the transfer to the refrigerator boxes containing the mineral salts and agar medium was carried out in a transfer chamber of the type shown in Fig. 4. The transfer chamber was first sterilized by atomizing propylene glycol on to an electric hot plate, maintained at a temperature of approximately 100°C. (Wade, 1947).

A simplified technique, which eliminates the transfer of strips from one desiccator to another, was subsequently developed. The strips to be sterilized are arranged loosely in a horizontal vacuum oven, fitted with a metal barrier so placed that the floor of the oven acts as a tray, and an outlet pipe flush with the floor of the oven. Methyl alcohol is poured into the bottom of the oven, which is then closed. The pressure is slightly reduced, and the temperature raised to 40°C. After four hours the pressure is restored to atmospheric by passing in air, which has been filtered through cotton wool. The outlet valve is opened and the methyl alcohol run out. The valve is then closed, the oven evacuated and maintained at 40°C. for one hour. After restoring the pressure to atmospheric, the oven is opened and the strips transferred to autoclaved refrigerator boxes containing the mineral salts and agar medium. This latter operation is carried out in a transfer hood which fits on to the end of the vacuum oven.

### 3. Soil Burial Method

According to this method, the fabric under test is buried in soil of definite moisture content and the effect on the strength of fabric determined. In the usual procedure the fabric is buried for a set period (Anon., 1942; Bertolet, 1944; United States Army, 1944) and then removed and the tensile strength determined, though Batson *et al.* (1944) considered it preferable to determine the time taken for the fabric to lose 85 per cent. of its strength, and a similar view is expressed by Dean *et al.* (1945).

Soil composted according to ordinary greenhouse practice has been used in all our tests. This soil has a high organic content, contains micro-organisms active in digesting cellulose, and has the texture of a sandy loam.

To determine the optimum moisture content for soil burial tests, using this soil, 12-oz. cotton duck strips were buried in soil at 40, 50, 60, 70, 80, and 90 per cent. of the water-holding capacity, and four strips from each removed after 4, 7, 11, and 14 days, and the tensile strength determined. The results are shown in Table 3 and are presented graphically in Fig. 5.

These results indicated that, when the moisture content was 50-70 per cent. of the W.H.C., there was little variation in loss of tensile strength, but with soil of 80 per cent. W.H.C. deterioration was more marked. The rate of loss of tensile strength at 90 per cent. W.H.C. was high during the first seven days, but then fell off rapidly. This effect is probably explained by the poor aeration of soil approaching saturation with water. Growth of micro-organisms (apart from

anaerobic bacteria) would therefore tend to decline because of accumulation of inhibiting materials, such as carbon dioxide, and because of depletion of oxygen from the soil.

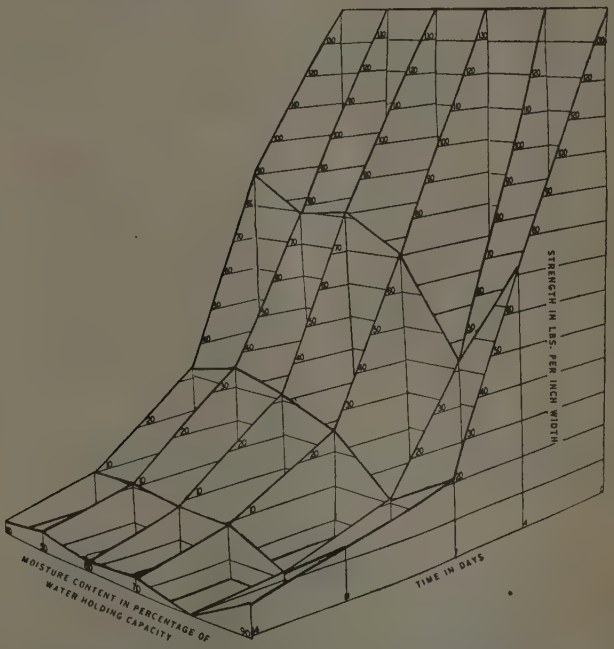


FIG. 5.—Effect of soil moisture content on rate of loss of strength of tensile strength of untreated cotton duck.

For routine tests, a soil moistened to 65-70 per cent. of its W.H.C. was used since it was found that if soil was moistened to the point when it felt moist when squeezed between the fingers, but would still crumble if dropped from a height of 1 foot on to the bench, it contained that amount of moisture. This rough test saved much time in determining moisture content accurately by drying and weighing the soil, and as the experiment quoted above demonstrates, a slight error in that region has little effect on the results.

The method adopted was to place a layer of the prepared soil of correct moisture content, 1 inch deep in the bottom of refrigerator boxes. The soil was compacted by tapping the box several times. The unsterilized fabric was pressed on to the soil, and a layer of soil half an inch deep placed above the strip and compacted. The refrigerator boxes were incubated at 30°C. for fourteen days, being weighed twice a week during incubation, and water added by spraying to replace any loss by evaporation. After removal from the soil, strips were washed with water, sterilized with methylated spirits, and dried; circles were washed and dried. The relevant physical tests were then carried out.

TABLE 3.—EFFECT OF SOIL MOISTURE CONTENT ON RATE OF LOSS OF TENSILE STRENGTH

| Number of Days Burial | Percentage Moisture Content | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 40 | | 50 | | 60 | | 70 | | 80 | | 90 | |
| | Log T.S. | T.S. | Log T.S. | T.S. | Log T.S. | T.S. | Log T.S. | T.S. | Log T.S. | T.S. | Log T.S. | T.S. |
| 4 .. .. .. .. .. .. | 1·96 | 91 | 1·91 | 81 | 1·91 | 81 | 1·86 | 72 | 1·64 | 44 | 1·83 | 68 |
| 7 .. .. .. .. .. .. | 1·53 | 34 | 1·59 | 39 | 1·52 | 33 | 1·44 | 28 | 0·98 | 9·5 | 1·34 | 22 |
| 10 .. .. .. .. .. .. | 1·08 | 12 | 1·12 | 13 | 1·03 | 11 | 1·01 | 10 | 0·44 | 3 | 1·19 | 16 |
| 14 .. .. .. .. .. .. | 0·71 | 5 | 0·82 | 7 | 0·65 | 4 | 0·69 | 5 | 0·00 | 1 | 0·94 | 9 |
| General Means for Moisture Content .. .. | 1·32 | 21 | 1·36 | 23 | 1·28 | 19 | 1·25 | 18 | 0·77 | 6 | 1·32 | 21 |

Since the range of the original figures was proportional to the means, they were converted to logarithms for analysis (Cochran, 1938). The value cited for tensile strength (T.S. lb. per inch width) in the table is the antilogarithm of the mean of the logarithms. The analysis of variance as described by Snedecor (1940) was applied with the following results :—

Difference for significance between general means of moisture content at 5 per cent. probability level (expressed as logarithms) .. .. .. .. .. .. .. .. .. .. .. .. 0·10

Difference for significance between general means of moisture content at 1 per cent. probability level (expressed as logarithms) .. .. .. .. .. .. .. .. .. .. .. .. 0·13

Difference for significance between sub-class means (individual entries in table) at 5 per cent. probability level (expressed as logarithms) .. .. .. .. .. .. .. .. .. .. .. .. 0·20

Difference for significance between sub-class means (individual entries in table) at 1 per cent. probability level (expressed as logarithms) .. .. .. .. .. .. .. .. .. .. .. .. 0·26

Overseas procedures demand that fabric be immersed to a depth of 5 inches, probably to ensure constant moisture content and temperature. It was considered that this precaution was only necessary in tests under greenhouse conditions, or when the moisture content was not controlled. The use of a shallow depth of soil allows better aeration of the soil, and is more economical of space.

## 4. Discussion

There is considerable difference of opinion as to the value of the various laboratory methods of assessing the resistance to attack by micro-organisms. This is discussed by Barker *et al.* (1943).

Soil burial seems the logical method for testing such materials as sandbags and cordage, which would normally come into contact with soil during service. Some workers, however, consider that soil burial or soil suspension methods are of more significance than pure culture tests for all materials. From results obtained here, it seems probable that most materials which withstand soil burial would also withstand pure culture tests, though cases have been noted when the loss of waterproofness in the *Aspergillus niger* test was greater than in soil burial tests. However, soil burial would be likely to eliminate treatments that would give good results on materials which do not normally come in contact with soil. A similar view has been expressed by Dean *et al.* (1945). In service, tentage materials do, on occasions, become contaminated with mud, but it is doubtful whether soil burial is comparable to such contamination. The soil suspension method developed by Furry and Zametkin (1943) would appear to approximate more closely to such conditions. Although some workers have found difficulty in reproducing results in soil burial tests, we have found it fairly satisfactory in this respect, though close agreement between different laboratories cannot perhaps be expected.

One of the strongest objections to the pure culture tests is that fungi more tolerant to fungicides than the test organisms may be encountered in the field. For this reason, workers should not restrict their attention to one or two fungi.

Whatever type of test is used, some physical determination such as loss of tensile strength or waterproofness should be used as the criterion. The amount of visible growth, which has formed the basis of some specifications, may be entirely misleading, and it has been found that vigorous growth of fungi is not always accompanied by loss of waterproofness, nor is the absence of macroscopically visible growth always an indication that waterproofness has not been reduced.

It is probable that the failure to obtain complete correlation between laboratory tests and performance in the field is due in large measure to inadequate conditioning treatments. Our laboratory washing tests, while apparently severe, did not cause the loss of as much mercury as mild weathering. Washing tests described in overseas specifications and literature generally consist of 24 hours' washing in water at 30°C. In our tests a longer washing time was employed, though the temperature was lower. However, tests of this nature are suspect since they do not reproduce the alternate wetting and drying which occurs in service.

For testing new materials it would therefore be desirable to expose treated pieces to natural weathering before submitting them to laboratory tests. Exposure under tropical conditions would be preferable, though valuable results may also be obtained under temperate conditions.

## 5. Acknowledgments

The mycological work described was conducted at the Plant Research Laboratories of the Victorian Department of Agriculture.

The physical determinations were made at the Munitions Supply Laboratories, Maribyrnong. The work described formed part of a cooperative investigation conducted by the Department of Munitions and the Victorian Department of Agriculture, and much of the work has been described in a hitherto restricted report (Cox *et al.*, 1945).

Mr. J. E. Cummins, who was Director of the Scientific Liaison Bureau at the time the work was conducted, assisted by providing some of the equipment for mycological testing, made overseas reports on current work available, and showed active interest in the progress of the work.

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# Effect of Some Micro-organisms on the Physical Properties of Cotton Duck

*By G. C. Wade, M.Agr.Sc.**

*Summary*

The effects of a number of fungi on the tensile strength and waterproofness of treated and untreated cotton duck are compared.

*Metarrhizium* sp. was the most active species tested, in reducing tensile strength of untreated duck. *Memnoniella echinata, Stachybotrys atra,* and *Chaetomium globosum* were also shown to be very strong cellulose digesters.

Various *Aspergillus* and *Penicillium* species were shown to reduce the waterproofness of the cotton duck.

## 1. Introduction

During the war period, numerous specimens of tentage which exhibited either loss of strength or waterproofness were received from the New Guinea area. These samples were examined for the presence of moulds and a considerable number of species isolated. Those species isolated frequently from deteriorated materials, or those related to species known to cause loss of tensile strength or waterproofness, were tested for those properties. Certain of the fungi which were very active in reducing tensile strength were compared carefully to assess their value for laboratory tests on rotproofness of cotton fabrics.

## 2. Effect on Loss of Tensile Strength

### (i) *Method*

The tests were conducted using an accelerating medium essentially as described by Thom *et al.* (1934) and with the formula:—

| | |
|---|---|
| Sodium nitrate | 3·0 g. |
| Potassium phosphate | 1·0 g. |
| Potassium chloride | 0·25 g. |
| Magnesium sulphate | 0·25 g. |
| Agar | 10·0 g. |
| Water | 1,000 ml. |

A layer of the medium about ¼ inch deep was poured into the bottom of refrigerator boxes. Strips of cotton duck each 2⅛ inches wide and 11 inches long, cut in the direction of the warp, were suspended above the agar by folding over glass rods, which were prevented from slipping by a small piece of rubber, and the boxes then autoclaved.

After autoclaving, the cotton threads holding the strips were cut and the strips pushed down in uniform contact with the agar, for a length of four inches (see Wade, 1947*b*, Figs. 1 and 2). The work was conducted in a transfer chamber sterilized with propylene glycol aerosol (Wade, 1947*a*).

* Now an officer of the Tasmanian Department of Agriculture; the work described was carried out while the author was on the staff of the Victorian Department of Agriculture and a member of the Mycological Panel of the Scientific Liaison Bureau.

The strips were then inoculated by spraying, by means of a de Vilbiss atomizer, with a spore suspension of the organism tested. The boxes were incubated at a temperature of 28–30°C. for fourteen days, and the tensile strength determined.

(ii) *Results*

The results of tests with a number of organisms are shown in Table 1. The figures given are the average of three or more readings. As the tests were not all conducted at the same time, the figures are not strictly comparable, but only give an indication of the activity of the organisms.

TABLE 1

| Organism | Effect on Appearance of Duck | Percentage Loss in Strength |
|---|---|---|
| *Actinomyces* sp. .. | Cream discolouration of duck. Strong earthy odour produced | 80 |
| *Aspergillus niger* .. | Black growth over surface of duck | Nil |
| *Bacterium* (Isolate A) | No discolouration .. .. | 50 |
| *Bacterium* (Isolate B) | No discolouration .. .. | 70 |
| *Chaetomium* sp. (probably *C. globosum*) | Yellow discolouration of duck. Abundant dark-grey perithecia formed on surface | 95 |
| *C. globosum* (culture from U.S.A.) | Yellow discolouration of duck. Abundant dark-grey perithecia formed on surface | 95–100 |
| *Chaetomium* sp. (isolated from sandbag) | Yellow discolouration of duck. Abundant dark-grey perithecia formed on surface | 80 |
| *Cladosporium* sp. . | Greenish-black discolouration of duck. No surface growth | 30–50 |
| *Curvularia* (*Brachysporium*) sp. | Brown discolouration of duck. Little surface growth | 85 |
| *Fusarium* sp. (*Roseum* section) | White surface growth .. | 25 |
| *Hormodendron* sp. .. | Reddish-purple discolouration of duck. Slight white and brown surface growth | 85 |
| *Memnoniella echinata* | Copious black mould growth over surface of duck | 100 |
| *Metarrhizium* sp. (culture from U.S.A.) | Black moist growth over surface of duck | 100 |
| *Penicillium* sp. (sclerote producing form) | No observable effect .. .. | Nil |
| *Penicillium luteum* .. | Green surface growth. Slight orange discolouration of duck | Nil |
| *Pestalozzia* sp. . | Grey discolouration of duck. Black spore masses on surface of duck | 30–50 |
| *Pullularia pullulans* .. | No observable effect .. .. | 5–15 |
| *Stachybotrys atra* .. | Copious dull-black growth over surface of duck | 100 |
| Sterile fungus—*Rhizoctonia* type | Dark-grey discolouration of duck. No surface growth | 80–95 |
| *Trichoderma* sp. .. | Fabric not discoloured. White surface growth with olive green spore masses | 15 |

*Curvularia* (*Brachysporium*) sp. and the sterile fungus were very frequently isolated from tentage from the New Guinea area, and the brownish or grey irregular patches caused by them were the most

common type of damage noted on samples obtained from the area. However, as the results show, they were less active in reducing strength of cotton duck than several other fungi, particularly *Memnoniella echinata, Stachybotrys atra,* and certain of the *Chaetomium* isolates. Their growth rate was slower than those latter species, and they produced spores less abundantly, so that it was difficult to obtain uniform results following inoculation with them. Therefore they were not used in routine rotproofing tests.

Of the very active cellulose-digesters, *Memnoniella echinata* was isolated most frequently. It was particularly common on tentage from very humid situations. *Stachybotrys atra* was not common on tentage from New Guinea but was commonly isolated from deteriorated cellulosic materials from the Melbourne area.

*Hormodendron* sp. was isolated from reddish purple areas on duck. Such areas were fairly frequent on duck from similar situations to those showing infection with *Curvularia* sp. and the sterile fungus, and it was similar in its capacity to digest cellulose.

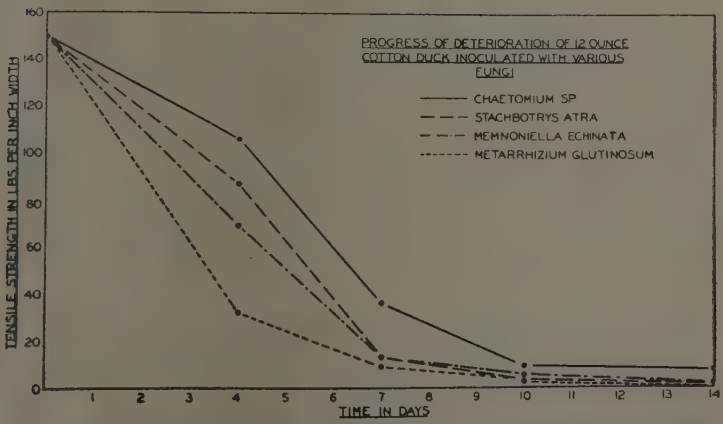


FIG. 1.—Progress of deterioration of 12-oz. cotton duck inoculated with various fungi (the curve for *Chaetomium globosum* has been omitted because there was no significant difference between the effect of this fungus and *Memnoniella echinata*).

*Pestalozzia* sp. was almost universally present on tentage from New Guinea, but as the results show, it is not a particularly active cellulose digester.

*Pullularia pullulans* was isolated particularly readily from samples of tentage, which had been treated by the copper soap—hot wax method, and which had shown extreme loss of strength after use in New Guinea. However, inoculation of duck with *P. pullulans* resulted in little growth, and it seems likely that the loss of strength of the samples from which it was isolated was primarily due to light-tendering. It is therefore not known why *Pullularia* was so consistently associated with this type of breakdown.

Thaysen and Bunker (1927) give descriptions of many of these fungi and a bibliography of micro-organisms attacking cellulose.

The data quoted in Table 1 only give an approximate indication of the relative activity of the fungi in digesting cellulose. In order to determine this more accurately for five of the most active forms, a further test was conducted in a similar manner, but four strips were removed after incubation for 4, 7, 10, and 14 days. The growth of the organisms was stopped immediately by immersing the strips in methylated spirits, and the tensile strengths were then determined.

The results are shown in Table 2, and illustrated graphically in Fig. 1.

*Metarrhizium* sp. caused more rapid deterioration than the other fungi tested. This result is consistent with the work of Greathouse *et al.* (1942). Deterioration was least rapid with *Chaetomium* sp. and there was no significant difference between the effects of *S. atra, M. echinata,* and *C. globosum.*

### 3. Relative Effect of Fungi on Tensile Strength of Rotproofed Cotton Duck

Tests were conducted to determine the relative effects of *M. echinata* and *S. atra* on duck treated by various processes. In these tests the fabric was sterilized by methyl alcohol vapour as described in a previous paper (Wade, 1947*b*). The results are shown in Table 3. There was no significant difference in the activity of *M. echinata* and *S. atra* on the copper treated fabrics tested, except in the case of unwashed caustic soda modified copper treated ducks, when *M. echinata* was more active. It is of interest to note that Jensen (1946) found that *M. echinata* is slightly more copper tolerant than *S. atra.* However, *M. echinata* caused significantly greater loss of strength of duck, finished to the American specification J.Q.D. 242, than did *S. atra.*

### 4. Effect of Various Fungi on Waterproofness of Cotton Duck

It has been known for a considerable time that a number of common moulds, particularly *Aspergillus* spp. and *Penicillium* spp. are capable of growing on cotton duck (Hardy, 1942; Thaysen and Bunker, 1927). The presence of these fungi was considered objectionable for aesthetic reasons, but their possible effect on other properties of the duck has apparently not been studied previously.

During the work conducted here, it was noted than these fungi grew vigorously on both untreated and copper soap treated cotton duck. Dr. H. L. Jensen, Macleay Bacteriologist, Linnean Society of New South Wales, independently noted this fact, and work first carried out by Dr. Jensen and the Munitions Supply Laboratories showed that *Aspergillus niger* was capable of causing loss of waterproofness of copper soap treated fabric (Jensen, 1946).

Tests were then conducted to determine the effect of a number of fungi on the waterproofness of untreated cotton duck.

#### (i) *Method*

Four-inch squares of untreated 18-oz. cotton duck were suspended above water in glass jars. The jars were then sterilized by autoclaving, and the duck inoculated by spraying with spore suspensions

TABLE 2.

| Number of Days Incubation | *Metarrhizium* sp. | | *Stachybotrys atra* | | *Memnoniella echinata* | | *Chaetomium globosum* | | *Chaetomium* sp. | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Log. T.S. | T.S. | Log. T.S. | T.S. | Log. T.S. | T.S. | Log. T.S. | T.S. | Log. T.S. | T.S. |
| 4 .. .. | 1·49 | 31 | 1·94 | 87 | 1·84 | 69 | 1·79 | 62 | 2·03 | 107 |
| 7 .. .. | 0·94 | 9 | 1·13 | 13 | 1·13 | 17 | 1·19 | 16 | 1·56 | 36 |
| 10 .. .. | 0·54 | 3 | 0·59 | 4 | 0·71 | 6 | 0·79 | 6 | 0·99 | 10 |
| 14 .. .. | 0·27 | 2 | 0·23 | 2 | 0·29 | 2 | 0·29 | 2 | 0·89 | 8 |
| General Means for Fungi | 0·81 | 6·5 | 0·97 | 9 | 1·01 | 10 | 1·01 | 10 | 1·37 | 23 |

Since the range of the original figures was proportional to the means, they were converted to logarithms for analysis. The value cited for tensile strength (T.S., lb. per in. width) in the table is the antilogarithm of the means of the logarithms. The analysis of variance technique described by Snedecor was applied in analysing the results.

Difference for significance between general means for fungi at 5 per cent. probability level (as logarithms) = 0·09.

Difference for significance between general means for fungi at 1 per cent. probability level (as logarithms) = 0·12.

Difference for significance between sub-class means (individual entries in table) at 5 per cent. probability level (expressed as logarithms) = 0·18.

Difference for significance between sub-class means (individual entries in table) at 1 per cent. probability level (expressed as logarithms) = 0·24.

TABLE 3.

| Nature of Fabric | Treatment | Tensile Strength, lb. per in. Width | | |
|---|---|---|---|---|
| | | Before Inoculation | After Inoculation and Incubation with *S. atra* | After Inoculation and Incubation with *M. echinata* |
| 12 oz. duck .. .. | Copper soap-wax emulsion .. .. .. .. | 137 | 104 | 80* |
| 12 oz. duck .. .. | Copper soap double bath— | | | |
| | As received .. .. .. .. | 162 | 174 | 170* |
| | After washing 7 days in a water spray .. .. | 167 | 139 | 133* |
| 18 oz. duck .. .. | Copper soap double bath (caustic soda modified)— | | | |
| | As received .. .. .. .. .. | 170 | 180 | 128† |
| | After washing 7 days in a water spray .. .. | 186 | 179 | 180† |
| 12 oz. duck .. .. | Copper tannate (factory process) .. .. .. | 176 | 90 | 84* |
| 18 oz. duck .. .. | Phenyl mercuric acetate .. .. .. .. | 192 | 199 | 206* |
| 12 oz. duck .. .. | Material nominally finished to specification J.Q.B. 242 .. | 193 | 201 | 105‡ |

* No significant difference between effects of the two fungi.

† Difference for significance at 5 per cent. probability level 7 and at 1 per cent. level 11.

‡ Difference for significance at 5 per cent. probability level 30 and at 1 per cent. level 45.

of a number of fungi. After incubation for 14 days, the waterproofness, in terms of the head of water required to produce leakage, was determined at the Munitions Supply Laboratories. The experiment was conducted in quadruplicate.

(ii) *Results*

The results are shown in Table 4.

TABLE 4.—EFFECT OF VARIOUS FUNGI ON THE WATERPROOFNESS OF 18-OZ. DUCK

| Organism | Waterproofness | Remarks |
|---|---|---|
| *Aspergillus niger* .. | ½ | Vigorous black surface growth |
| *A. penicilloides* .. | ½ | Vigorous green surface growth |
| *A. ustus* .. .. | 2 | Vigorous buff surface growth |
| *A. glaucus* .. .. | 1 | Moderate green surface growth |
| *A. flavus* .. .. | 2 | Vigorous yellow-green surface growth |
| *A. sydowi* .. .. | 8 | No obvious growth |
| *Penicillium luteum* .. | 3½ | Vigorous green surface growth |
| *Pestalozzia* sp. .. | 5 | Grey stained irregular areas |
| *Memnoniella echinata*. | 7 | Vigorous black surface growth |
| *Cladosporium* sp. .. | 9 | Greenish-black diamond shaped areas. No surface growth |
| Uninoculated .. | 10 | |

Difference for significance at 5 per cent. probability level = 1·5.
Difference for significance at 1 per cent. probability level = 2·0.

*Aspergillus niger, A. penicilloides, A. ustus, A. glaucus,* and *A. flavus* caused extensive loss of waterproofness. Although *Cladosporium* sp. and *Memnoniella echinata* grew vigorously on the duck, they did not cause marked loss of waterproofness.

The reason for the effect of these fungi on waterproofness has not been definitely established, but it is probable that they destroy the oils and waxy materials normally present on the surface of the fibres. It is suggestive that the most active fungi are members of the *Aspergillus* and *Penicillium* genera, which have the ability to break down fats and oils (Horowitz-Wlassowa and Liwschitz, 1935), and that Eyre (1932) showed that *A. niger* and *A. flavus* were more powerful in breaking down fats and oils than *A. sydowi.*

### 5. Effect of Fungi on Waterproofness of Rotproofed Cotton Duck

(i) *Method*

Four-inch circles of the treated duck were sterilized by exposure to methyl alcohol vapour, and then rested on the mineral salts and agar medium described earlier in this report. They were then inoculated by spraying with spore suspensions of the fungi. After incubation for 14 days at 30°C., the waterproofness was determined.

(ii) *Results*

The results are shown in Table 5 and demonstrate that both *Aspergillus ustus* and the *Penicillium* sp. are more mercury tolerant than *A. niger. A. ustus* appears from these results to be slightly more copper sensitive than *A. niger* or *Penicillium* sp.

TABLE 5.

| Nature of Fabric | Treatment | Waterproofness, inches, after Inoculation with— | | |
|---|---|---|---|---|
| | | *A. niger* | *A. ustus* | *Penicillium* sp. |
| 18-oz. duck .. .. | Phenyl mercuric acetate (0·017 per cent. mercury on fabric)— | | | |
| | As received .. .. .. .. .. | 8 (n.a.) | 0 (m.) | 8 (v.sl.) |
| | After washing .. .. .. .. .. | 6 (v.sl.) | 0 (v.) | ½ (v.) |
| 12-oz. duck .. .. | Copper soap double bath (soda ash modified)— | | | |
| | As received .. .. .. .. .. | ½ (v.sl.) | 3 (v.sl.) | ½ (sl.) |
| | After washing .. .. .. .. .. | 0 (m.) | 0 (m.)* | ½ (v.) |

Results are the means of four determinations—

n.a. = No apparent growth.
v.sl. = Very slight growth.
m. = Moderate growth.
v. = Vigorous growth.

* Copper soap showed moderate decolourization.

## 6. Acknowledgments

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Mr. J. E. Cummins, former Director of the Scientific Liaison Bureau, assisted with the work in many ways, particularly by making available overseas reports written during the war period and by his active interest in the work.

Miss G. E. McQuienn and Miss N. M. Fenwick-Barbour, formerly of the staff of the Munitions Supply Laboratories, assisted capably with the laboratory work.

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# Fusarium Wilt of Tomato in Australia

## 2. Inheritance of Field Immunity to Fusarium Wilt in the Tomato (*Lycopersicon esculentum*)

*By E. M. Hutton, M.Sc.,* Margaret Mills, B.Sc.,* and J. E. Giles†*

*Summary*

It has been shown that Pan America is a suitable parent for introducing field immunity to Fusarium wilt into new tomato hybrids suited to Australian conditions. The use of Pan America in some crosses leads to an improvement in vitamin C content.

Simple crosses have resulted in the incorporation of field immunity in suitable hybrids but multiple crosses containing Pan America in two places are recommended.

The inheritance mechanism for field immunity, although a simple one, does not follow the usual course, and appears to be influenced by both the female and pollen parent used.

### 1. Introduction

Previous work (Mills and Hutton, 1946) suggested that strains of *Fusarium bulbigenum* var. *lycopersici* of varying pathogenicity existed in Australia. It was demonstrated that *Lycopersicon pimpinellifolium* and the variety Pan America derived from it by Porte and Walker (1941) are highly resistant to all the Australian isolates of the organism tested. This high degree of resistance to the development of the organism results in field immunity to Fusarium wilt in Pan America.

Inheritance of immunity to Fusarium wilt in hybrid progenies has been studied by Bohn and Tucker (1940) who found that immunity depended on a single dominant genetic factor. From crosses they developed hybrids homozygous for immunity and having good agronomic quality. Porte and Walker (1941) using similar methods produced Pan America.

In Australia, Pan America, although producing good quality fruit, is a poor yielder under most conditions, and has not been generally accepted by growers. The work summarized in this paper shows that the field immunity to Fusarium wilt of Pan America is heritable, and that by using it as a parent, field immune hybrids suitable to Australian conditions can be developed by plant breeders.

### 2. Materials and Methods

Inoculation methods were similar to those used previously (Mills and Hutton, 1946). Five-weeks-old tomato seedlings were inoculated by dipping the roots in a water suspension of macerated mycelium and spores of a highly pathogenic strain of *Fusarium bulbigenum* var. *lycopersici* grown on a modified Tochnai medium. The seedlings were planted in pots in the greenhouse, and 28 days after inoculation were rated on the extent of vascular browning (internal rating), as this method had been shown less liable to error than rating based on the outward appearance of the plant. Average internal ratings of Bonny Best and Pan America checks used throughout the experiment were 8·1 and 0·76 respectively. Table 1 gives a comparison between some of the Bonny Best and Pan America checks.

* An officer of the Division of Plant Industry.

† An officer of the Commonwealth Research Station, Merbein.

TABLE 1.—INTERNAL RATINGS OF FUSARIUM INOCULATED BONNY BEST AND PAN AMERICA CHECKS

| Variety | Number of Plants rated Internally as— | | | | | | | | | | | Total | Percentage Rated 0–2 | Percentage Rated 3–10 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 0 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | | | |
| Bonny Best .. | 1 | 5 | 8 | 8 | 14 | 8 | 27 | 24 | 50 | 64 | 130 | 339 | 4·1 | 95·9 |
| Pan America .. | 184 | 180 | 17 | 3 | 4 | .. | 2 | 7 | .. | .. | .. | 397 | 96·0 | 4·0 |

0–2 Vascular browning absent or confined to root system.
3–10 Vascular browning extending upwards in the stem.

In the majority of Bonny Best plants vascular browning extended towards the tops. These plants and hybrids of similar susceptibility were rated internally from 3–10 and were classed susceptible to Fusarium wilt. Vascular browning did not extend above ground level in most Pan America plants which were thus rated 0–2 as shown in Table 1. Pan America and plants in hybrid progenies given this rating do not wilt if left growing in the greenhouse and so are classed as having field immunity to Fusarium wilt.

A number of crosses using the field immune Pan America were made at Canberra. For comparison, an F4 selection of a cross between *L. pimpinellifolium* and Marglobe received as 42–50–6 from Dr. B. L. Wade of United States of America, has been used as the field immune parent in other crosses. The susceptible varieties used in the Canberra crosses varied in resistance to Fusarium wilt and were grouped previously (Mills and Hutton, 1946).

### 3. Inheritance of Field Immunity to Fusarium Wilt in the Progeny of Crosses

(i) *Crosses between Susceptible Parents*

TABLE 2.—NUMBERS OF FIELD IMMUNE AND SUSCEPTIBLE PLANTS IN THE PROGENY OF CROSSES BETWEEN SUSCEPTIBLE PARENTS

| Variety | No. of Lines | Generation | Field Immune | Susceptible | Total |
|---|---|---|---|---|---|
| Rouge de Marmande (R.D.M.) x Pearson 29–17 .. .. .. | .. | F2 | 38 | 215 | 253 |
| Rouge de Marmande (R.D.M.) x Pearson 29–17 .. .. .. | 5 | F3 | 31 | 169 | 200 |
| Rouge de Marmande (R.D.M.) x Pearson 29–17 .. .. .. | 2 | F4 | 1 | 44 | 45 |
| Vetomold (V.) x Rouge de Marmande (R.D.M.) .. .. .. | 1 | F3 | .. | 19 | 19 |
| Pearson x Earliana .. .. | 6 | F3 | 4 | 114 | 118 |
| Bounty x 926–142–1 (Wade) .. | 7 | F3 | 10 | 283 | 293 |
| Tatinter x 926–142–1 (Wade) .. | 11 | F3 | 4 | 434 | 438 |
| Tatura Dwarf Globe x 926–142–1 (Wade) | 10 | F3 | 11 | 407 | 418 |
| (V. x R.D.M.) x Riverside .. .. | 3 | F3 | .. | 53 | 53 |
| [V. x R.D.M.) x Pearson .. .. | 6 | F3 | .. | 106 | 106 |
| (R.D.M. x Pearson 29–17) x R.D.M. | .. | F1 | .. | 89 | 89 |
| | | | 99 | 1,933 | 2,032 |

Table 2 shows that the majority of plants in hybrid progenies from crosses between susceptible parents are field susceptible. Most of the field immune segregates are in the Pearson 29–17 cross, indicating that if sufficient hybrid work were done with this less susceptible parent, field immune hybrids of good agronomic quality might be produced. It is considered that a large proportion of the field immune plants in Table 2 come within the experimental error, since 4 per cent. of Bonny Best plants are classed as field immune in Table 1.

(ii) *Crosses between a Field Immune and Susceptible Parent*

The results in Table 3 show that in the first generation field immunity is completely dominant over susceptibility.

TABLE 3.—NUMBERS OF RESISTANT AND SUSCEPTIBLE PLANTS IN THE F1 OF CROSSES BETWEEN SUSCEPTIBLE PARENTS AND THE FIELD IMMUNE PARENTS PAN AMERICA AND 42–50–6 (Wade)

| Variety | Generation | Field Immune | Susceptible | Total |
|---|---|---|---|---|
| Bounty x Pan America (P.A.) .. | F1 | 40 | .. | 40 |
| Tatinter x P.A. .. .. .. | F1 | 20 | .. | 20 |
| Bounty x 42–50–6 .. .. | F1 | 81 | .. | 81 |
| Tatinter x 42–50–6 .. .. | F1 | 88 | 1 | 89 |
| | | 229 | 1 | 230 |

Tables 4 and 5 show the numbers of field immune and field susceptible segregates in the F2 and more advanced progenies of crosses between the susceptible varieties Rouge de Marmande, Bounty, Tatinter, and Tatura Dwarf Globe, and the field immune male parents Pan America and 42–50–6 (Wade). The F2 progenies, were tested in the greenhouse without field selection. All other progenies, with the exception of one, resulted from agronomic selections in the field. The exception is the F3 progeny marked G.H. in the Rouge de Marmande x Pan America cross. This resulted from F2 plants not given an internal rating and which did not succumb to Fusarium wilt in the greenhouse.

TABLE 4.—NUMBERS OF RESISTANT AND SUSCEPTIBLE PLANTS IN THE PROGENY OF CROSSES BETWEEN A FEMALE SUSCEPTIBLE PARENT AND THE FIELD IMMUNE MALE PARENT PAN AMERICA

| Variety | No. of Lines | Generation | Field Immune | Susceptible | Total |
|---|---|---|---|---|---|
| R.D.M. x Pan America (P.A.) .. | .. | F2 | 438 | 57 | 495 |
| R.D.M. x Pan America (P.A.) .. | 17 | F3 | 564 | 104 | 668 |
| R.D.M. x Pan America (P.A.) .. | 20 G.H. | F3 | 323 | 28 | 351 |
| R.D.M. x Pan America (P.A.) .. | 5 | F4 | 454 | 68 | 522 |
| R.D.M. x Pan America (P.A.) .. | 5 | F5 | 321 | 34 | 355 |
| Bounty x P.A. .. .. .. | .. | F2 | 79 | 17 | 96 |
| | 1 | F3 | 1 | 42 | 43 |
| Tatinter x P.A. .. .. .. | .. | F2 | 405 | 29 | 434 |
| | 8 | F3 | 277 | 74 | 351 |
| Tatura Dwarf Globe x P.A. .. | .. | F2 | 317 | 38 | 355 |
| | 2 | F3 | 59 | 19 | 78 |
| | | | 3,238 | 510 | 3,748 |

The important points illustrated by Tables 4 and 5 are the preponderance of field immune plants in most progenies and the high proportion of agronomic field selections with immunity to Fusarium wilt. The greater than 3 : 1 ratios of field immune to field susceptible plants in the F2's are difficult to explain on the basis of the operation of a single dominant gene as shown by Bohn and Tucker (1940). A simple type of inheritance must be involved since Table 3 shows dominance to be complete in the F1. Bohn and Tucker (1940) noted a number of cases with a higher proportion of immune progeny than expected when the Fusarium immune parent was the male. To explain this they considered the factor for immunity to be linked with a factor influencing the effectiveness of the microgamete. It is possible that the greater than 3 : 1 ratios in Tables 4 and 5 could be explained on this basis as in all instances the field immune parents Pan America and 42–50–6 were used as the male. No reciprocal crosses of those in Tables 4 and 5 were made so that the hypothesis of Bohn and Tucker (1940) could not be fully tested. The preponderance of the field immune factor is more marked when 42–50–6 (Wade) is used as the pollen parent. There is some indication that different female susceptible parents may influence the number of field immune progeny produced in crosses with field immune male parents, so that modifying factors may be operating.

TABLE 5.—NUMBERS OF RESISTANT AND SUSCEPTIBLE PLANTS IN THE PROGENY OF CROSSES BETWEEN A FEMALE SUSCEPTIBLE PARENT AND THE FIELD IMMUNE MALE PARENT 42–50–6 (Wade)

| Variety | No. of Lines | Generation | Field Immune | Susceptible | Total |
|---|---|---|---|---|---|
| Bounty x 42–50–6 | | F2 | 346 | 2 | 348 |
| | 3 | F3 | 89 | 42 | 131 |
| Tatinter x 42–50–6 | | F2 | 373 | 15 | 388 |
| | 3 | F3 | 127 | 4 | 131 |
| Tatura Dwarf Globe x 42–50–6 | | F2 | 469 | 39 | 508 |
| | 4 | F3 | 143 | 40 | 183 |
| | | | 1,547 | 142 | 1,689 |

The excess of resistant types makes the problem of combining agronomic suitability and field immunity to Fusarium wilt easier. In the Rouge de Marmande-Pan America cross of Table 4, the F2 had a preponderance of field immune plants, so that a high proportion of the seventeen F3 lines field selected for agronomic quality had the immune character. Inoculation in the greenhouse showed that eight lines were homozygous for field immunity, seven heterozygous for field immunity, one heterozygous susceptible, and one homozygous susceptible. Of the twenty F3 lines selected from the F2 in the greenhouse for field immunity, nine were homozygous and eleven heterozygous for this character. On this basis it does not appear advantageous to select the F2 in the greenhouse for field immunity to Fusarium wilt. The inheritance pattern of field immunity to Fusarium wilt is maintained throughout the different generations of the Rouge de Marmande-Pan America cross and the other crosses of Tables 4 and 5. That its basis is sound is shown by the fact that field immune hybrids evolved by this technique have remained free from Fusarium wilt under conditions of widespread field infection of susceptible varieties.

(iii) *Multiple Crosses Including One or Two Field Immune Parents*

Table 6 gives the numbers of field immune and susceptible plants occurring in the progenies of multiple crosses containing one and two field immune parents respectively. The second cross containing both 42–50–6 (Wade) and Pan America gave the greatest numbers of resistant parents. Multiple crosses like the first in Table 6 are of little practical use as it would be difficult to select the desired combination of agronomic quality and field immunity to Fusarium wilt from the progenies.

TABLE 6.—NUMBERS OF FIELD IMMUNE AND SUSCEPTIBLE PLANTS IN MULTIPLE CROSSES INVOLVING ONE OR TWO RESISTANT PARENTS

| Variety | Generation | Field Immune | Susceptible | Total |
|---|---|---|---|---|
| (V. x R.D.M. x Pearson 29–17) x (V. x R.D.M. x P.A.) .. .. | F2 | 25 | 473 | 498 |
| (42–50 x V. x R.D.M.) x (V. x R.D.M. x P.A.) .. .. .. | F2 | 438 | 105 | 543 |
| | | 463 | 578 | 1,041 |

## 4. Field Performance of Fusarium Wilt Immune Hybrids Developed from the Crosses

Table 7 gives the field performance in the C.S.I.R. plots at Red Cliffs, Victoria, of some of the advanced hybrids showing field immunity to Fusarium wilt. These hybrids were developed from the crosses shown in Tables 4, 5, and 6. In the trial plots 16 plants of each variety or hybrid were randomized in each of six blocks so that 96 plants of each were transplanted. During the 1946-47 season Fusarium wilt was prevalent so that the yielding ability in lb. per plant in Table 7 reflects to some extent the resistance to Fusarium wilt of the various varieties and hybrids. Pearson 29–17 has been the outstanding variety in replicated trials at Red Cliffs over a number of years and is taken as the standard by which new varieties or hybrids are evaluated.

Of the advanced hybrids in Table 7, 7A–2–1, 12A–1–1, 12A–6–1, and 12A–8–1 yielded more heavily than Pearson 29–17, none of the differences being statistically significant. On the basis of first grade fruit over 2½ in. in diameter, 7A–2–1, 12A–6–1, and 12A–8–1 gave higher yields than Pearson 29–17, the differences lacking significance as before. The hybrids 5A–3–1, 5A–4–1, and 12A–7–1 were still segregating a number of Fusarium wilt susceptible plants, whereas the other hybrids were almost fixed for field immunity although showing segregation for agronomic type.

In Table 7, Pearson 29–17 is among the lowest in vitamin C content. This is in accord with previous results from replicated trials carried out for several years at Red Cliffs. In these, Pearson 29–17, Rouge de Marmande, and Adelaide Dwarf Red have given average vitamin C contents from 35–38 mg. per 100 g., whereas Pan America, Grosse Lisse, and Riverside have ranged from 45 to 48 mg. per 100 g. Pan America

has usually been the best variety for vitamin C. The results in Table 7 indicate that the high vitamin C content of Pan America is heritable, since the last four hybrids, particularly 12A–7–1 and 12A–8–1, are among the best in this respect. At the second harvest all the advanced hybrids had significantly greater vitamin C contents than Pearson 29–17.

TABLE 7.—YIELD AND VITAMIN C CONTENT OF FUSARIUM WILT IMMUNE HYBRIDS IN COMPARISON WITH STANDARD VARIETIES AT RED CLIFFS, 1946-47 SEASON

| Variety | Cross | Weight of Fruit lb./plant | | | Average Vitamin C Content in mg./100 g. | |
|---|---|---|---|---|---|---|
| | | Fruit over 2¼ in. diam. | Fruit less than 2¼ in. diam. | Total | 1st Harvest | 2nd Harvest |
| Adelaide Dwarf Red | .. .. .. | 2·7 | 1·1 | 4·9 | 41·75 | 39·57 |
| Pearson 29–17 .. | .. .. .. | 4·4 | 3·1 | 9·1 | 38·07 | 30·49 |
| Riverside .. .. | .. .. .. | 3·0 | 1·5 | 6·4 | 45·08 | 47·39 |
| Red Cloud .. | .. .. .. | 3·1 | 1·2 | 6·3 | 43·90 | 40·25 |
| 5A–3–1 .. .. | Rouge de Marmande x 42–50 (Wade) | 0·5 | 3·9 | 7·7 | 35·65 | 43·25 |
| 5A–4–1 .. .. | Rouge de Marmande x 42–50 (Wade) | 0·6 | 2·5 | 5·2 | 35·34 | 45·54 |
| 7A–2–1 .. .. | (Vetomold x R.D.M.) x Pan America | 4·8 | 3·2 | 9·9 | 27·19 | 43·64 |
| 10A–4–1 .. .. | (Vetomold x R.D.M.) x 42–50–6 (Wade) | 0·3 | 3·6 | 8·1 | 39·76 | 45·34 |
| 12A–1–1 .. .. | R.D.M. x Pan America .. | 1·7 | 5·8 | 9·7 | 40·14 | 46·46 |
| 12A–6–1 .. .. | R.D.M. x Pan America .. | 5·0 | 3·4 | 11·0 | 43·29 | 42·27 |
| 12A–7–1 .. .. | R.D.M. x Pan America .. | 3·5 | 1·5 | 6·8 | 54·33 | 46·79 |
| 12A–8–1 .. .. | R.D.M. x Pan America .. | 4·8 | 3·0 | 10·4 | 50·08 | 46·41 |

*In yield* min. diff. for significance at 5 per cent. point = 2·8 lb.
*In vitamin C* min. diff. for significance at 5 per cent. point = 8·04 mg.

## 5. Discussion

For plant breeders, the important point shown by this paper is the relative ease with which the combination of field immunity to Fusarium wilt and good agronomic quality can be achieved by the use in crosses of the easily available variety Pan America. It appears that with its use hybrids with yields as good as standard varieties can be developed. There is also the possibility of an improvement in vitamin C content with Pan America hybrids.

The preponderance of field immune segregates in the crosses described is a puzzling feature of the work. Until further experiments are done it is not possible to understand fully the mechanism involved. Until proved otherwise, it is best to use Pan America as the pollen parent. The work described gives an indication of the results that can be expected with different types of crosses. The backcross method has not been used as it is considered that, with the possible exception of Pearson 29–17, most of the standard varieties need agronomic improvement as well as improvement in disease resistance qualities.

Although the simple cross involving a susceptible and field immune parent has been largely used for the purpose of this paper it is possibly not the best type of cross for the plant breeder to use. Multiple crosses as shown in Table 6 including four or more varieties have a greater chance of improving the tomato agronomically as well as introducing field immunity to Fusarium wilt. It is well known that many of the desirable agronomic characters are dependent on the operation of multiple factors, so that improvements in agronomic type are more likely to result from multiple crosses containing several varieties with the desirable characters. Where multiple crosses are used, it is apparent that to introduce field immunity to Fusarium wilt in a sufficient proportion of segregates, Pan America should occur in at least two places.

Where field immunity to Fusarium wilt is being introduced into the segregates of crosses, agronomic field selection should be followed by a test of field immunity to the disease by a greenhouse technique along the lines described. It is inadvisable to rely on selection for immunity to the disease under conditions of field infection, as the development of Fusarium wilt in plants growing in the field is greatly influenced by environmental conditions.

## 6. Acknowledgments

Messrs. R. D. Brock and R. R. Rochford of the Division of Plant Industry were responsible for the data obtained in the later stages of this work. Mr. J. Webster of the Council's Commonwealth Research Station, Merebin, kindly made available his vitamin C figures for the hybrids and varieties in the Red Cliffs trials. Mr. G. McIntyre statistically analysed the data from this trial.

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# The Sub-surface Atmosphere of Wheat Infested with *Rhizopertha dominica* F.

*By R. F. Powning, A.S.T.C.**

*Summary*

The results of some studies on the composition of the sub-surface atmosphere and insect distribution in Victorian bulk-wheat depots are presented, together with data from laboratory experiments.

In laboratory studies, the carbon dioxide concentration reached 15 to 20 per cent. when an infestation of *Rhizopertha dominica* F. was started either at the surface or deep in the wheat contained in tall narrow jars. A surface infestation distributed itself evenly through the wheat and produced a large number of second generation adults, but any insects leaving the vicinity of the wheat surface were killed. The insects in a deep infestation showed no tendency to migrate away from the high carbon dioxide concentration in the bottom of the jar, some surviving an atmosphere of between 10 per cent. and 18 per cent. carbon dioxide for eight weeks—but there was an almost complete absence of second generation adults.

Analyses of the intergranular atmosphere of stored bulk-wheat did not reveal gases other than the normal constituents of air. Carbon dioxide increased owing to respiration processes within the wheat bulk, and the oxygen varied in a complementary manner. In the heavily infested wheat, the carbon dioxide concentration rose to about 2·5 per cent. in the vicinity of the maximum insect population (consisting mainly of *Rhizopertha dominica* F.). The temperature of both infested and uninfested wheat varied in the same manner as the carbon dioxide.

## 1. Introduction

The restriction of the insect infestation to the periphery of bulk-wheat has been described by Wilson (1945*a*), and it has been shown that the phenomenon may be satisfactorily explained by the presence of unsuitable temperature-humidity conditions beneath the wheat surface (Wilson, 1945*a*, 1947; Birch, 1945). However, before the true explanation had been demonstrated, it was thought that the apparently uninhabitable zone in the wheat might be due to toxic constituents in the intergranular air. Abnormal carbon dioxide or oxygen concentrations were considered likely to be contributing factors, and the data obtained in analyses of the sub-surface atmosphere of stored bulk-wheat are presented in this paper.

The laboratory experiments described in the next section were undertaken to determine, under somewhat simplified conditions, the nature and extent of the changes in the intergranular atmosphere caused by a developing insect population, and the effect of these changes on that population.

## 2. Laboratory Studies

### (i) *Experimental Technique*

*Rhizopertha dominica* F., being the most serious pest in bulk-wheat in Victoria, was chosen for these laboratory experiments, which were planned as complementary studies to the field experiments. The test insects were 0-7 days old and reared in the

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laboratory under controlled conditions. The experiments were carried out at 90°F. (32°C.) and 65 per cent. R.H. in cylindrical glass jars, 5 ft. tall by 3 in. internal diameter, filled to the top with conditioned wheat and covered with fine wire gauze lids. To facilitate the insect counts, discs of wire gauze, of sufficiently large gauge to permit free movement of the insects, were inserted at one foot intervals in the jars as they were filled; lengths of ¼-in. glass tubing, embedded in the wheat to the appropriate depth, served for drawing the gas samples. Infestations were initiated by the addition of 500 adult insects to either the top or the bottom of the jars. In both series of experiments observations were made on separate jars after periods of 3, 7, and 10 days, and 2, 4, 6, and 8 weeks, the population count terminating each experiment.

A Haldane gas analysis apparatus was used for the carbon dioxide analyses, samples being taken in duplicate and their mean used for the graphs. Each foot of wheat was examined separately for live and dead insects, the results being recorded as histogram blocks in the illustrations.

(ii) *Carbon Dioxide Bulid-up in Insect-free Wheat*

As a check on carbon dioxide production in wheat by micro-organisms or by the respiration of the wheat itself, two jars were set up with wheat of low moisture content (9·24 per cent.) and two with wheat of relatively high moisture content (11·4 per cent.). One of each of these was hermetically sealed, the other left open, and the intergranular air analysed for carbon dioxide after a four-week period at 90°F. (32°C). The sealed relatively moist wheat produced a concentration of 2·4 per cent. carbon dioxide, but both of the jars containing dry wheat and the unsealed jar with the moist wheat developed less than 0·5 per cent.

This is in agreement with figures quoted by Dendy and Elkington (1920) who showed, when using a smaller quantity of a dry wheat under slightly different conditions, that the concentration of carbon dioxide after seven days was 0·48 per cent.

(iii) *Behaviour of a Surface Infestation*

When placed on the surface, the insects showed a strong tendency to move downwards, and in a few days live insects were found in all depths of the wheat. After about four weeks, there was little further insect movement and a high mortality occurred together with the high carbon dioxide concentration which had reached 15-20 per cent.

When it was found that anomalous carbon dioxide figures, not comparable with the smooth trends shown in the other experiments, were revealed in the four-weeks experiments, this was repeated (four weeks B). The histograms show that, although the total insect population and its distribution was much the same as in the original four-weeks jar, only those insects which remained near the surface survived. The only explanation that can be offered for this difference is that, for some reason, breeding in the first jar is subnormal and irregular, whereas in the duplicate jar normal numbers of late-stage larvae were present, which might be expected to raise the carbon dioxide concentration markedly. Howe and Oxley (1944) have shown that fourth instar larvae of *Calandra* produce more than three times as much carbon dioxide as any other stage, and it is possible that a similar relation exists in *Rhizopertha.*

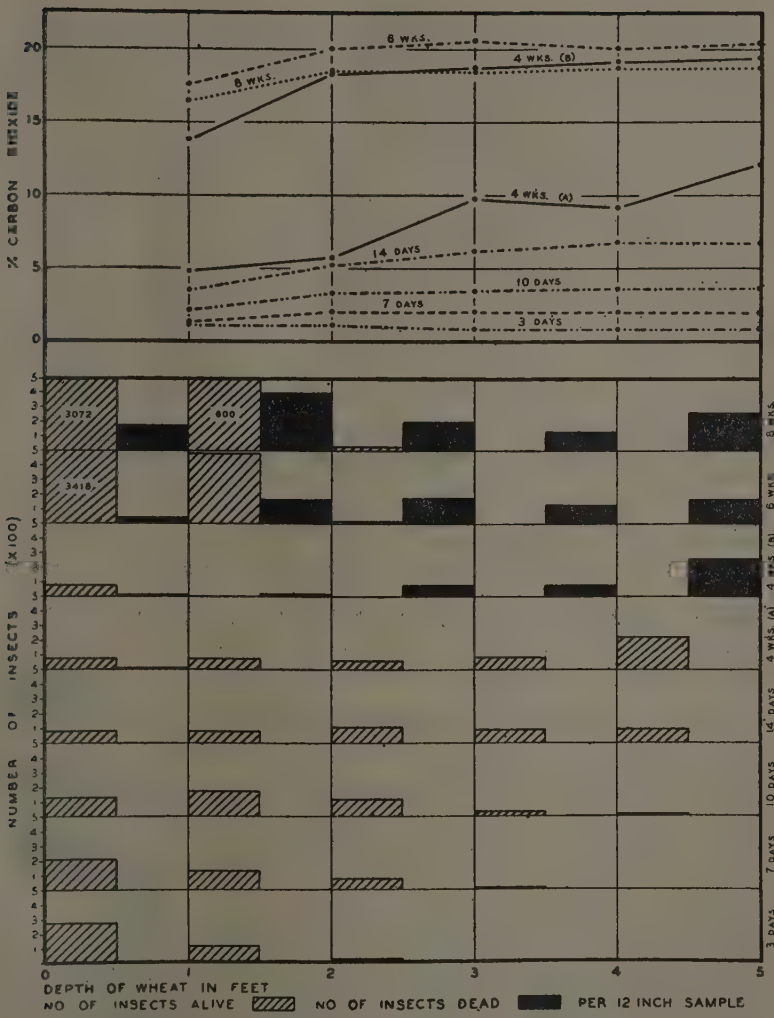



FIG. 1.—Changes in carbon dioxide concentration and insect distribution in tall glass jars when infested at the surface with *Rhizopertha dominica* F.

(iv) *Behaviour of a Deep Infestation*

In the deep infestation there was an immediate increase in carbon dioxide concentration in the lower parts of the jar, but the insects showed no tendency to migrate up through the wheat away from it. All the insects lived in an atmosphere of 10-15 per cent. carbon dioxide for 11 days, and some were alive after 8 weeks in an atmosphere of 10-18 per cent. carbon dioxide.

Contrary to the results of the surface infestation, very little breeding occurred under these conditions, the counts indicating an absence of second generation adults at six weeks; in the eight-weeks count the increase was only about 30 per cent.

### 3. Studies in Bulk-wheat Depots

(i) *Experimental Technique*

The war-time bulk-wheat storage depots in Victoria consisted of two huge sheds, each about 1,000 ft long by 200 ft. wide, in which the wheat, to the extent of several million bushels, formed a continuous heap, retained by bulkheads of heavy timber. Infestation

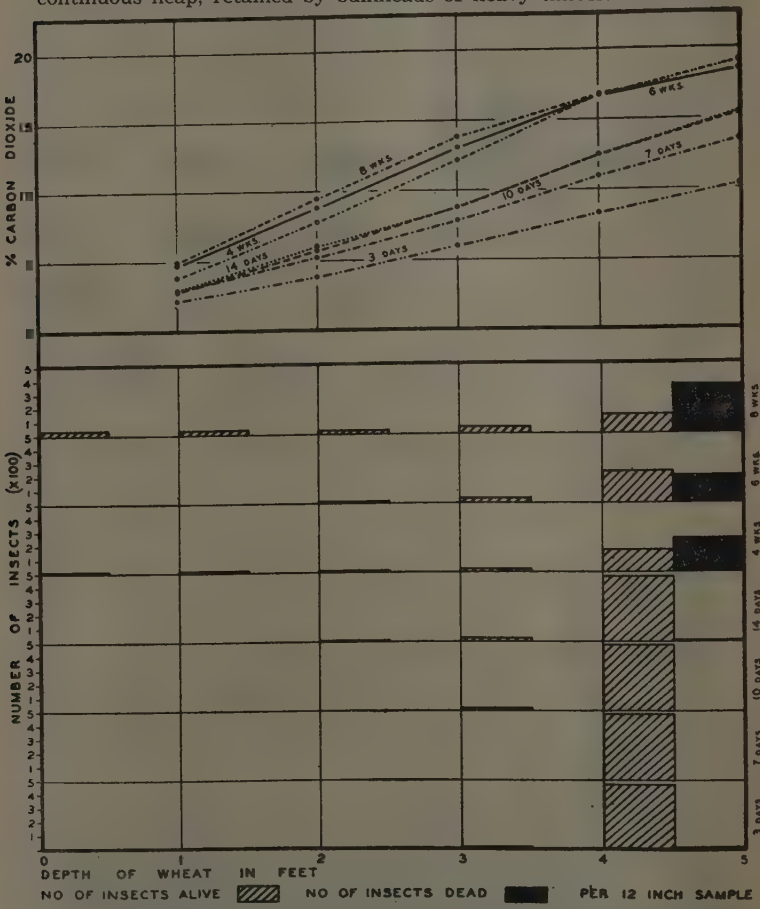



FIG. 2.—Changes in carbon dioxide concentration and insect distribution in tall glass jars when infested at the bottom with *Rhizopertha dominica* F.

consisted mainly of *Rhizopertha dominica* F., but in certain situations, considerable numbers of *Latheticus oryzae* Waterh. and small numbers of other insects were present (Wilson, 1945*b*).

In selecting sites for the collection of the analytical data, areas that had been recently fumigated or that were close to a bulkhead or the crest were avoided. The gas samples were taken at the centre of an infested area with the aid of a levelling bulb and suitable lengths of $\frac{1}{8}$-in. diameter copper tubing. The analyses were carried out with a Sleigh portable gas analysis apparatus.

Temperatures at various depths in the wheat were determined by thermometers attached to wooden probes. A special metal probe of 1-in. internal diameter, subdivided into 6-in. sections, was used for sampling the grain at different depths and determining the distribution of the insect population. The numbers of live and dead insects separated from the samples so obtained are included in the form of histograms in Figs. 3 and 4.

(ii) *Results of Observations and Analyses*

Typical sets of figures are presented to illustrate the variations in carbon dioxide, oxygen, temperature, and insect numbers with depth of wheat. They were obtained from:—

(*a*) Insect-free wheat, 1942-43 season, "No. 6 Pool" (15-18 months in storage); and 1943-44 season, "No. 7 Pool" (3-6 months in storage).

(*b*) A light infestation. 1941-42 season (27-30 months in storage).

(*c*) A medium infestation. 1941-42 season (27-30 months in storage).

(*d*) A heavy infestation. 1941-42 season (27-30 months in storage).

In both lots of insect-free wheat (Fig. 3*a*) the temperature and the carbon dioxide rose gradually from a low value near the surface to become constant below about 3 feet, but, while the curves were similar, the 1943-44 wheat was slightly cooler and had a lower carbon dioxide concentration.

With the appearance of a light infestation (Fig. 3*b*) the character of both the carbon dioxide and the temperature curves changed markedly. Insects were found throughout the whole depth sampled, but most of them were concentrated within 18 inches of the surface. This distribution was reflected in an increase in the percentage of carbon dioxide and the temperature, the oxygen concentration showing a corresponding decrease.

In Figs. 4*a* and 4*b* are presented data from a medium and a heavy infestation respectively. The insects were more numerous, though fewer at depths below two feet than in the light infestation. The graphs of carbon dioxide and temperature show much higher values, and the oxygen concentration is lower, than in Fig. 1*b*, but the curves are essentially similar, i.e., the maxima and minima occur at a depth in the wheat corresponding to the position of highest insect population.

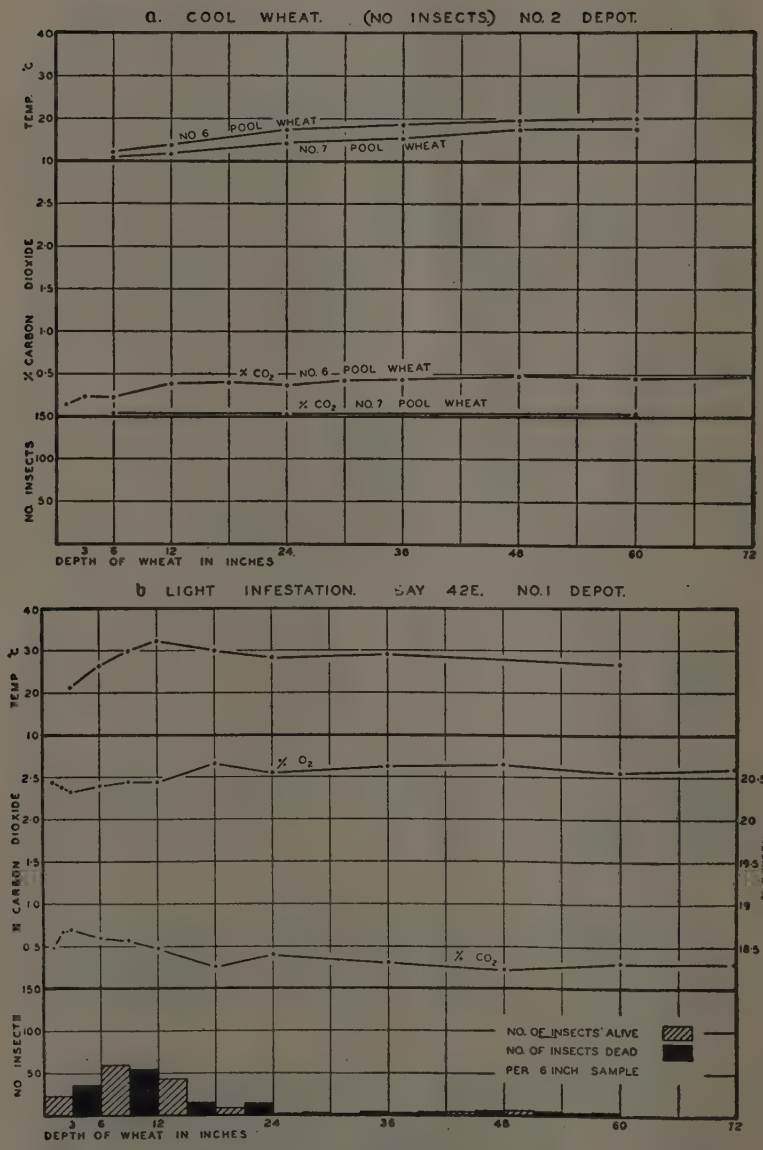
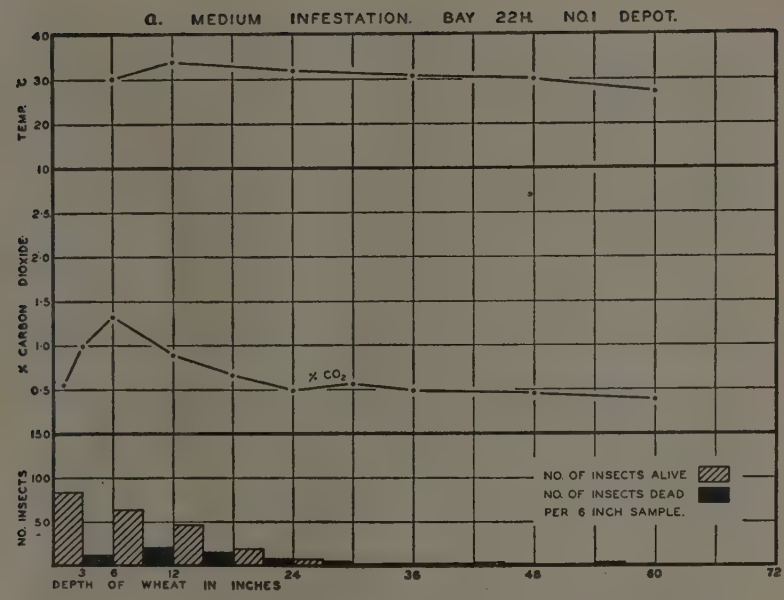



FIG. 3.—(*a*) Variation in carbon dioxide concentration and temperature with depth in cool uninfested wheat.

(*b*) Variation in carbon dioxide and oxygen concentration, temperature and insect numbers in a light infestation.



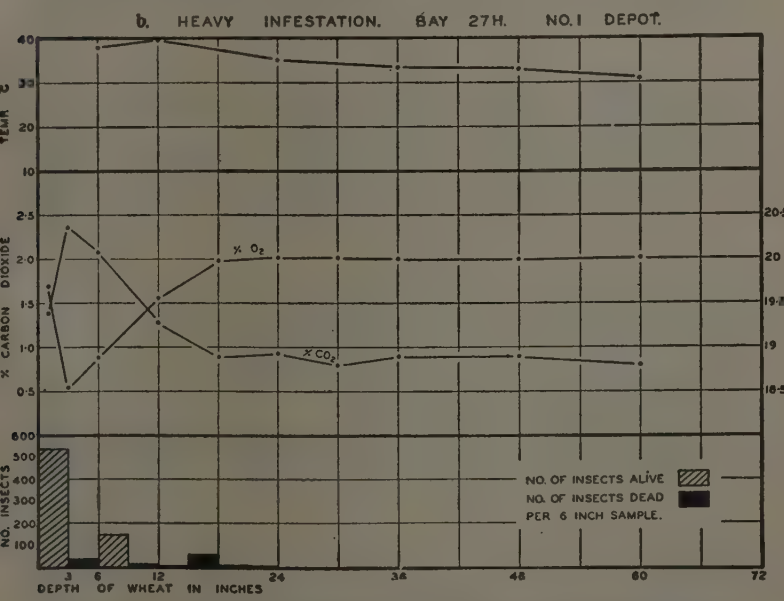




FIG. 4.—(*a*) Variation in temperature, carbon dioxide concentration, and insect numbers in wheat with a medium infestation.

(*b*) Variation in temperature, carbon dioxide and oxygen concentrations, and insect numbers in heavily infested wheat.

## 4. Discussion

It is reported that in Western Australian depots where infestations generally are much more severe than in the Victorian depots, carbon dioxide concentrations of about 5 per cent. occurred (Wilson, 1945*c*). Oxley and Howe (1944) made many determinations of carbon dioxide in intergranular air of infested grain, and found that the concentration was normally less than 1 per cent. They also state, however, that where the infestation is heavy, and a considerable bulk of wheat is heating, concentrations of 4-5 per cent. may occur. In Victoria, a large number of analyses were carried out on samples from wheat under various conditions of infestation, but on no occasion was the carbon dioxide concentration higher than 3 per cent., or the oxygen figure more than 3 per cent. below normal. Analyses for carbon monoxide, aldehydes, and hydrocarbons showed that these were not present in the intergranular atmosphere.

The tolerance of *Rhizopertha* to high carbon dioxide concentrations (5-10 per cent.) and the rather surprising absence of any reaction on the part of the insects to a gradient of carbon dioxide concentration, confirm the validity of Wilson's conclusion that the limitation of insect infestations to the periphery of bulk wheat is adequately explained by temperature and humidity conditions that develop within the grain mass.

## 5. Acknowledgments

The author wishes to thank Mr. F. Wilson and Mr. F. J. Gay for their willing advice and cooperation.

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# The Addition of Skim Milk Powder to Australian Bread

*By R. C. Hutchinson,* D.Sc., H. E. West,† B.S.A., and Jeanette T. Jeffreys**

*Summary*

Typical Australian skim milk powders were incorporated in test doughs on a 6 per cent. dry matter basis. The resultant loaves were immature, the volumes poor, the crusts harsh, and the crumbs coarse, open, and with frequent cores. Unsuccessful attempts were made to eliminate these defects by subjecting the milk to various treatments and by using flour from harder wheats.

Skim milk powders that were known to have excellent baking qualities under United States conditions were also incorporated in test doughs where they were found to have the same depressing effect on the resultant loaves as the Australian powders.

In Australia it is not customary to add cane sugar or fat to the common loaf but, in the United States, both these constituents are used. Baking tests were therefore conducted on doughs containing each and both of these constituents. The results of these tests showed that, when small amounts of fat are added to doughs containing skim milk powder, the resultant loaves are greatly improved. Furthermore, it was found that a loaf, superior in all respects to the water-loaf control, could be obtained by adding the fat in the form of an emulsion. Several fats were tested.

Test bakes were also conducted on doughs containing skim milk powder, fat, and small amounts of several surface-modifying ingredients and on doughs containing various German whole egg and egg albumen substitutes made from skim milk. The loaves resulting from all these bakes were inferior to those containing skim milk powder and fat in the form of an emulsion.

As a result of baking tests with skim milk powders containing several fats in different percentages, it was concluded that satisfactory results could be obtained with a powder containing 20 per cent. fat and that the most desirable amount of powder to add to bread was 12½ per cent.

The results of several large scale baking tests in which skim milk powder, containing 20 per cent. mutton fat, was used on 12½ per cent. dry matter basis are briefly described. In general, these results confirmed those obtained in the laboratory.

## 1. Introduction

There is no article of food so generally and universally consumed as bread. In many countries it is the basic food of a large majority of the people and, if this bread is low in any important dietary constituent, the health of the people will almost certainly suffer in consequence. Unfortunately, ordinary white bread is a poor source of several essential food constituents which include the amino acids, lysine and tryptophane; calcium; and the vitamins riboflavin and thiamin. On the other hand, skim milk powder is a particularly good source of all these constituents and, by incorporating skim milk solids in bread, a loaf with a much higher nutritive value results.

In the United States, it is common practice to add 6 per cent. skim milk powder to bread, although rye bread only contains 4-5 per cent., whilst the standard school lunch loaf contains 12 per cent. and special high calcium loaves may contain as much as 40 per cent.

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In Australia, it is not customary to add skim milk powder to the common loaf, the only breads containing milk powders being fancy breads for which there is a limited demand. When skim milk powder is incorporated in the common Australian loaf, there is an appreciable reduction in volume, the crust is harsh and immature, and the crumb coarse, open, and with frequent cores. This is contrary to the results obtained in the United States where it is claimed that the addition of skim milk powder to bread improves every physical characteristic of the loaf.

The object of this investigation was to determine the reason for the detrimental effect which skim milk powder has on the physical properties of Australian bread and to determine whether this detrimental effect can be eliminated without losing any of the enhanced nutritive value of the bread or increasing appreciably its cost.

## 2. Experimental Test Bakes

(i) *Experimental Formula, Technique, and Evaluation*

During the investigation, many test bakes were conducted, and the formula for the control doughs, the baking technique, and the method of evaluating the finished loaves, are described hereunder.

(*a*) *Formula.*—The following formula was used:—

| | | |
|---|---|---|
| Flour | 300 g. | = 100 per cent. |
| Salt | 6 g. | = 2 per cent. |
| Compressed yeast | 5·4 g. | = 1·8 per cent. |
| Improver | 1 g. | = 0·33 per cent. |
| Water | variable | = 58-60 per cent. |

(*b*) *Technique.*—The yeast was first shaken with 30 cc. of water until a fine, homogeneous suspension was formed and the salt and improver dissolved in a further 144 cc. of water which had been heated to the temperature necessary to bring the temperature of the dough, after the mixing of all ingredients, to 26·6°C. (80°F.). All the ingredients were then mixed for two minutes in a laboratory model Hobart mixer during which time additional water was added if necessary. The dough was then placed in a jar in a fermentation cabinet held at 26·6°C. The jar was part of a closed system which permitted the measurement of the rate and degree of fermentation by the displacement of a saturated salt solution. When the displacement had reached 1,100 cc., and without breaking the closed system, the jar was knocked to assist the release of more gas and fermentation then allowed to continue until the total volume of gas evolved was 1,400 cc. Then 400 grams of dough were taken, "handed up," replaced in the fermentation cabinet for 10 minutes' recovery, moulded into a square mould, placed in a baking tin, and returned to the fermentation cabinet for proofing. During the proof period, the formation of a skin was prevented by keeping the atmosphere moist with steam. The dough was then placed in an oven at 221°C. (430°F.) for 25-30 minutes.

(*c*) *Evaluation.*—Sixteen hours after they were baked, all test loaves were scored in the following manner.

A water-loaf control, which was included in each batch baked, was used as a standard for comparison and given an arbitrary value of 100. Points, based on the following properties, were then allotted to each loaf:—(*a*) volume, (*b*) maturity, (*c*) crust characteristics, and (*d*) crumb characteristics. No definite values were ascribed to aroma or palatability although a constant watch was kept for abnormalities.

(ii) *Skim Milk Powder in Ordinary Australian Bread*

Six typical Australian skim milk powders, all of which had been bought on the open market, were incorporated in test doughs to the extent of 6 per cent. on a dry matter basis. The use of 6 per cent. skim milk powder provided milk solids equivalent to those which would have been provided had the entire liquid content of the dough been fresh skim milk. The powders were added dry and, with the exception of an increased fermentation time, there were no modifications in the baking technique. The results of these tests are given in Table 1. Fig. 1 is a diagrammatic representation of a section of the control loaf and of sections of two test loaves, one containing spray-dried and the other roller-dried powder. Both the loaves containing skim milk powder had similar physical properties.

TABLE 1.—THE EFFECT OF ADDING SKIM MILK POWDER TO AUSTRALIAN BREAD

| Reference Number | Powder | Bread Score |
|---|---|---|
| Control | | 100 |
| 1 | Spray-dried | 55 |
| 2 | Spray-dried | 50 |
| 3 | Spray-dried | 45 |
| 4 | Roller-dried | 45 |
| 5 | Roller-dried | 45 |
| 6 | Roller-dried | 45 |

From Table 1 it will be seen that the addition of skim milk powder, either spray-dried or roller-dried, produced a very inferior loaf. The volumes were poor, the control loaf having a volume of 1,420 cc. and the test loaves only 1,220 cc. The test loaves were also very immature, the crusts harsh, and the crumbs, coarse, open, and with frequent cores.

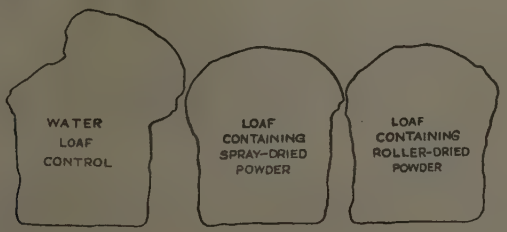




FIG. 1.

In further tests, the batter or ferment method of mixing doughs was employed. In this method a batter or ferment consisting of—

| | |
|---|---|
| Flour .. .. .. .. | 30 g. |
| Milk powder .. .. .. | 18 g. |
| Improver .. .. .. | 1 g. |
| Water at 49°C. .. .. .. | 20 cc. |
| Yeast solution at 32°C. .. .. | 34·5 cc. |

was allowed to ferment for one hour after which it was mixed in the usual way with the remaining flour, salt, and liquor. The dough was then fermented to 1,200-1,300 cc. of gas. The results of these tests are given in Table 2. From this table it will be seen that the batter or ferment method of mixing doughs containing skim milk powder was not as satisfactory as the method employed previously. The loaves were extremely immature and the volumes very poor.

TABLE 2.—THE ADDITION OF SKIM MILK POWDER TO BREAD PREPARED BY THE BATTER METHOD

| Reference Number | Powder | Bread Score |
|---|---|---|
| Control .. .. .. | .. .. .. .. | 100 |
| 7 .. .. .. | Spray-dried .. .. | 45 |
| 8 .. .. .. | Roller-dried .. .. | 40 |

(iii) *Preheated Skim Milk Powders*

The results of experiments conducted by Greenbank *et al.* (1927) indicated that the preheat treatment to which skim milk is subjected before being dried affects its baking qualities; powder which has received a relatively high heat treatment yields a loaf of greater volume and better texture than powder which has been subjected to a less severe heat treatment. The following year Grewe and Holm (1928) conducted more detailed baking tests in which they used three different flours, and spray-dried skim milk powders that had been preheated to 50°, 63°, 73°, 83°, 93°, and 100°C. for 30 minutes. With all flours, the poorest results were obtained in bread containing powder which had been subjected to a preheat treatment of 50°C. A preheat treament of 63°C. gave a slightly better result but there was a marked improvement in the loaves containing powders that had been preheated to 73°, 83°, 93°, and 100°C. Skovholt and Bailey (1931) found that preheat treatments at 77°, 88°, and 96°C. for 30 minutes greatly improved the baking qualities of skim milk powders and that the improvement was approximately the same for each treatment. In later experiments, Ashworth *et al.* (1942) used spray-dried powders which had been preheated at 82-88°C. (180-190°F.) for 30 minutes, and recently Harland, Ashworth, and Golding (1943) used powders which had been preheated to 82°C. for 45 minutes or 90-95°C. for 5 minutes.

Hence, it would appear that in the baking of bread the most satisfactory results are obtained from skim milk powders which have been preheated to a temperature of approximately 85°C. for 30 minutes or to a higher temperature for a shorter period.

During the manufacture of roller-dried powder, milk is first heated to a temperature of approximately 100·5°C. for about 10 minutes and then to approximately 120°C. for about 3 seconds. When milk is spray-dried, the heat treatment is less severe and depends upon the method of drying and the frequency with which the powder is removed from the drying chamber. In most Australian factories the temperature of the milk does not exceed 80°C. and the powder may not remain at this temperature for more than a few minutes.

In order to obtain samples which were known to have received adequate heat treatment, arrangements were made for the manufacture of four samples of powder from milk which had been specially preheated to 85°C. for 30 minutes. Three of the samples were spray-dried, the temperature of the drying chamber being 79-80°C., and the fourth was roller-dried at a steam pressure of 60 pounds per square inch. The first sample, which was from the first of the milk to be sprayed into the drying chamber at the beginning of the day's run, had remained in the chamber for approximately 14 hours before being collected. The second sample, which was from milk which had been sprayed into the drying chamber half way through the day's run, had remained in the chamber for approximately 7 hours before being collected. The third sample, which was from the last of the milk to be sprayed into the drying chamber before closing down for the day, had remained in the chamber for only a few minutes. When reconstituted all these powders had an acidity of 0·15 per cent. when expressed as lactic acid.

These powders were added to test doughs to the extent of 6 per cent. on a dry matter basis. They were added both wet and dry. When added wet, all liquor except that substracted for the yeast solution, was mixed with the milk powder and added to the flour in the form of a liquid. The results of the test bakes are given in Table 3. From this table, it will be seen that the additional preheat treatment did not improve the baking qualities of the powders. All the test loaves were very immature, the volumes poor, the crusts harsh, and the crumbs coarse, open, and with frequent cores.

TABLE 3.—THE ADDITION OF SPECIALLY PREHEATED SKIM MILK POWDERS TO BREAD

| Reference Number | Powder | Bread Score | |
|---|---|---|---|
| | | Addition Wet | Addition Dry |
| Control | | 100 | |
| 9 | Spray, 14 hrs. | 50 | .. |
| 10 | Spray, 14 hrs. | .. | 50 |
| 11 | Spray, 7 hrs. | 50 | .. |
| 12 | Spray, 7 hrs. | .. | 50 |
| 13 | Spray, sev. mins. | 45 | .. |
| 14 | Spray, sev. mins. | .. | 45 |
| 15 | Roller | 45 | .. |
| 16 | Roller | .. | 45 |

A sample of the second spray-dried powder was then reconstituted and portions of the reconstituted milk subjected to additional and more drastic heat treatments. These reconstituted milks were then added to test doughs so that each dough contained 6 per cent. skim milk solids on a dry matter basis. The results of the test bakes are given in Table 4. From these results it is evident that the additional heat treatment to which the reconstituted powders were subjected was not of great value in improving their baking qualities. There was only a slight improvement in volume and maturity.

TABLE 4.—THE ADDITION TO BREAD OF POWDERS SUBJECTED TO ADDITIONAL HEAT TREATMENTS

| Reference Number | Additional Treatment | Bread Score |
|---|---|---|
| Control | | 100 |
| 17 | 90° C. for 5 minutes | 55 |
| 18 | 95° C. for 5 minutes | 55 |
| 19 | 100° C. for 5 minutes | 50 |
| 20 | 110° C. for 5 minutes | 65 |
| 21 | 90° C. for 15 minutes | 55 |
| 22 | 95° C. for 15 minutes | 50 |
| 23 | 100° C. for 15 minutes | 55 |
| 24 | 90° C. for 30 minutes | 50 |
| 25 | 95° C. for 30 minutes | 55 |
| 26 | 100° C. for 30 minutes | 55 |

When skim milk was heated to temperatures higher than 110°C. for five minutes, or slightly less, the colour was so dark that it adversely affected the colour of the bread.

(iv) *Acidified Fresh Skim Milks*

The doughs containing skim milk had a pH of approximately 5·8 whilst the controls had a pH of approximately 5·2. This suggested that the acidity of the skim milk may be an important factor determining its baking quality.

Samples of fresh skim milk, which had been heated to temperatures of 100° and 110°C., and held at these temperatures for approximately five minutes, were acidified by the addition of various amounts of lactic acid and used in the preparation of eight test doughs. On a dry matter basis these doughs each contained 6 per cent. skim milk solids. The results of the test bakes are given in Table 5. From the results of this table, it will be seen that an increased acidity greatly improved the baking qualities of fresh skim milk when heated to temperatures of 100° or 110°C. Also, at the lower acidities, milk heated to 110°C. had better baking qualities than milk heated to 100°C. In loaves 19, 27, and 29 the volumes were poor, in loaves 20, 28, and 31 they were fair, in loaf 30 fair to good, and in loaf 32 good. Loaf 19 was very immature, loaves 20 and 27 only slightly immature, and the remaining loaves of average maturity. In loaves 19-29, the texture was open and slightly coarse but in the remaining loaves it was fine and even. In all loaves, the colour of the crumb was good but the colour of the crust rather high.

Although an increased acidity, together with a comparatively severe preheat treatment, improved greatly the baking qualities of fresh skim milk, the resultant loaves were still inferior to an ordinary water loaf.

TABLE 5.—THE ADDITION OF ACIDIFIED FRESH SKIM MILK TO BREAD

| Reference Number | Milk Acidity | Bread Score | |
|---|---|---|---|
| | | Heat Treatment at 100° C. | Heat Treatment at 110° C. |
| | % | | |
| Control .. .. | .. | 100 | |
| 19 .. .. .. | 0·17 | 50 | .. |
| 20 .. .. .. | 0·17 | .. | 65 |
| 27 .. .. .. | 0·31 | 60 | .. |
| 28 .. .. .. | 0·31 | .. | 70 |
| 29 .. .. .. | 0·39 | 65 | .. |
| 30 .. .. .. | 0·39 | .. | 85 |
| 31 .. .. .. | 0·50 | 85 | .. |
| 32 .. .. .. | 0·50 | .. | 85 |

(v) *Flours from Soft and Hard Wheats*

In all the foregoing bakes, a blend of average Victorian flours was used. These flours were milled mostly from soft wheats and, in order to investigate the effect of using a hard wheat flour, a blend containing 80 per cent. of hard, Queensland wheat flour was used. The results of bakes containing this flour are given in Table 6. In both loaves, the volumes were poor, the loaves slightly immature, and the crumbs open.

TABLE 6.—BREAD FROM HARD WHEAT FLOURS

| Reference Number | Powder | Bread Score |
|---|---|---|
| Control .. .. .. | .. .. .. .. | 100 |
| 33 .. .. .. | Spray-dried .. .. | 60 |
| 34 .. .. .. | Roller-dried .. .. | 50 |

(vi) *American Skim Milk Powders*

Samples of three skim milk powders, which were known to have excellent baking qualities under United States conditions, were next obtained from the American Dry Milk Institute in Chicago. Two of the samples had been spray-dried and one roller-dried. On a reconstituted basis, their acidities were 0·16, 0·16, and 0·17 per cent. respectively. These powders were added to doughs on a 6 per cent. basis, the doughs being made from the original blend of average Victorian flours. The results of the test bakes are given in Table 7.

From these results it is seen that, when added to Australian bread, American skim milk powders had the same depressing effect as Australian powders. The loaves were all very immature the volumes poor and the crumbs coarse, open, and with frequent cores.

TABLE 7.—THE ADDITION OF AMERICAN SKIM MILK POWDERS TO BREAD

| Reference Number | Powder | Bread Score | |
|---|---|---|---|
| | | Addition Wet | Addition Dry |
| Control | .. | 100 | |
| 35 | Spray 1 | 50 | .. |
| 36 | Spray 1 | .. | 50 |
| 37 | Spray 2 | 50 | .. |
| 38 | Spray 2 | .. | 50 |
| 39 | Roller | 50 | .. |
| 40 | Roller | .. | 50 |

(vii) *The Addition of Sugar and Fat to Bread*

The results of the preceding tests indicated that the depressing effect of skim milk powder on Australian bread was not due to any particular characteristic of the milk powder or the flour. It was suggested that it may be due to the fact that in Australia neither cane sugar nor fat is added to the common loaf whereas American breads contain both these ingredients. In order to investigate this point baking tests were conducted on doughs which contained (*a*) cane sugar plus additional fat, (*b*) cane sugar only, (*c*) additional fat only, and (*d*) neither cane sugar nor additional fat. On a dry matter basis, the cane sugar and additional fat were each added to the extent of 2 per cent. and the skim milk powder 6 per cent. The fat consisted of lard and all the additional ingredients were added dry. The results of the test bakes are given in Table 8.

TABLE 8.—THE ADDITION OF SKIM MILK POWDER, SUGAR, AND FAT TO BREAD

| Reference Number | Powder | Sugar | Fat | Bread Score |
|---|---|---|---|---|
| Control | .. | − | − | 100 |
| 1 | Spray | − | − | 55 |
| 4 | Roller | − | − | 45 |
| Control | .. | + | − | 100 |
| 41 | Spray | + | − | 60 |
| 42 | Roller | + | − | 45 |
| 43 | Spray | + | − | 55 |
| 44 | Roller | + | − | 45 |
| Control | .. | − | + | 100 |
| 45 | Spray | − | + | 90 |
| 46 | Roller | − | + | 80 |
| 47 | Spray | − | + | 90 |
| 48 | Roller | − | + | 80 |
| Control | .. | + | + | 100 |
| 49 | Spray | + | + | 90 |
| 50 | Roller | + | + | 80 |
| 51 | Spray | + | + | 90 |
| 52 | Roller | + | + | 80 |

From the results in Table 8, it will be seen that, although sugar hastens fermentation time, it is of little value in improving the physical quality of bread. In all the loaves containing sugar there were definite signs of immaturity, the volumes were poor and the texture open, coarse, and with numerous cores. On the other hand, the addition of fat improved the physical quality to a marked degree and, in all the loaves containing fat, there was an increase in volume, the loaves were of average maturity, and the textures even, although inclined to be "fuzzy."

(viii) *The Addition of a Fat Emulsion to Bread*

In the preceding bakes, the fat was mixed into the dough in the same way as the other ingredients. In the bakes which are about to be described, the fat was added in the form of an emulsion.

This emulsion contained the following constituents:—

| | |
|---|---|
| Skim milk powder .. | 180 g. |
| Sugar .. .. | 60 g. |
| Salt .. .. | 60 g. |
| Lard .. .. | 60 g. |
| Water .. .. | 360 g. |

and each dough contained 72 grams. From the results presented in Table 9 and Fig. 2, it will be seen that, when lard is added in the form of an emulsion, the resultant loaves are greatly improved, being definitely superior to the control loaf. For both spray and roller dried powders, the loaves were of average maturity and the volumes good. In each loaf the texture was also good, although inclined to be slightly "fuzzy" in the loaf containing roller-dried powder.

TABLE 9.—THE ADDITION OF A LARD EMULSION TO BREAD

| Reference Number | Powder | Bread Score |
|---|---|---|
| Control .. .. .. | .. .. .. .. | 100 |
| 53 .. .. .. | Spray-dried .. .. | 115 |
| 54 .. .. .. | Roller-dried .. .. | 105 |

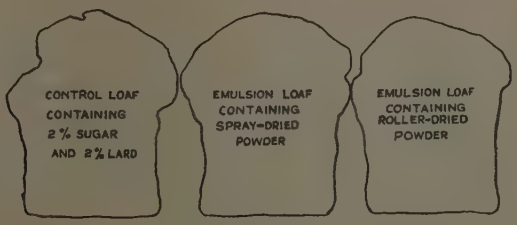


FIG. 2.

In order to investigate, in greater detail, the effect of adding fat to bread containing skim milk powder, tests were conducted in which lard was either directly mixed into the dough or added as an emulsion.

The method of adding the milk powders, which had been previously studied, was also varied, the addition being made dry, wet, or as part of the emulsion. The results are presented in Table 10. From these results, it is evident that there was no, or little, differences in breads containing lard that had been mixed into doughs to which skim milk powder had been added in the dry and wet forms. When the lard and milk powder were added in the form of an emulsion, however, there was a marked improvement. In the loaves containing milk powders in the wet and dry forms, there was slight immaturity, the volumes ranged from fair to good, and, in general, the crumbs were soft, fine, and even, although inclined to be slightly open in the first and last bakes. When lard and milk powder were added in the form of an emulsion, the loaves were of average maturity, there was a marked improvement in the volume, the crumb was soft, fine, and even, and only in the last bake was there any inclination to openess.

TABLE 10.—THE ADDITION OF LARD TO BREAD

| Reference Number | Powder | Addition | Bread Score |
|---|---|---|---|
| Control | .. .. .. .. | .. .. .. | 100 |
| 55 | American Spray, 1 .. .. | Dry .. .. | 90 |
| 56 | American Spray, 1 .. .. | Wet .. .. | 90 |
| 57 | American Spray, 1 .. .. | Emulsion .. .. | 110 |
| 58 | American Spray, 2 .. .. | Dry .. .. | 90 |
| 59 | American Spray, 2 .. .. | Wet .. .. | 90 |
| 60 | American Spray, 2 .. .. | Emulsion .. .. | 110 |
| 61 | American Roller .. .. | Dry .. .. | 95 |
| 62 | American Roller .. .. | Wet .. .. | 95 |
| 63 | American Roller .. .. | Emulsion .. .. | 120 |
| 64 | Spray, 14 hrs. .. .. | Dry .. .. | 90 |
| 65 | Spray, 14 hrs. .. .. | Wet .. .. | 90 |
| 66 | Spray, 14 hrs. .. .. | Emulsion .. .. | 110 |
| 67 | Spray, 7 hrs. .. .. | Dry .. .. | 90 |
| 68 | Spray, 7 hrs. .. .. | Wet .. .. | 90 |
| 69 | Spray, 7 hrs. .. .. | Emulsion .. .. | 115 |
| 70 | Spray, sev. mins. .. .. | Dry .. .. | 80 |
| 71 | Spray, sev. mins. .. .. | Wet .. .. | 80 |
| 72 | Spray, sev. mins. .. .. | Emulsion .. .. | 110 |
| 73 | Roller .. .. .. | Dry .. .. | 80 |
| 74 | Roller .. .. .. | Wet .. .. | 80 |
| 75 | Roller .. .. .. | Emulsion .. .. | 105 |

So far lard had been the only fat used, but, in Australia, there are four other common edible fats or oils each of which deserves consideration. These are beef fat, mutton fat, peanut oil, and maize oil. The results of baking tests in which 2 per cent. of these fats have been added to doughs containing 6 per cent. spray-dried skim milk powder are given in Table 11. The plasticity of the hydrogenated oils was approximately equal to that of lard.

From the results in Table 11, it will be seen that for all the fats and hydrogenated oils, the best results were obtained with the fats in the form of an emulsion. The beef suet emulsion gave the best results although good results were obtained with beef fat, mutton

fat, mutton suet, and hydrogenated peanut and hydrogenated maize oil emulsions. It is interesting to note that neither unhydrogenated peanut nor maize oil gave improved results when added in the form of emulsions. In no loaf was there any noticeable difference in palatability or aroma due to the presence of the additional fat.

TABLE 11.—THE ADDITION OF VARIOUS FATS AND OILS TO BREAD

| Reference Number | Fat or Oil | Addition | Bread Score |
|---|---|---|---|
| Control | .. .. .. .. | .. .. .. | 100 |
| 76 | Beef fat .. .. .. | Dry .. .. | 95 |
| 77 | Beef fat .. .. .. | Emulsion .. .. | 110 |
| 78 | Beef suet .. .. .. | Dry .. .. | 100 |
| 79 | Beef suet .. .. .. | Emulsion .. .. | 115 |
| 80 | Mutton fat .. .. .. | Dry .. .. | 95 |
| 81 | Mutton fat .. .. .. | Emulsion .. .. | 105 |
| 82 | Mutton suet .. .. .. | Dry .. .. | 100 |
| 83 | Mutton suet .. .. .. | Emulsion .. .. | 110 |
| 84 | Peanut oil .. .. .. | Dry .. .. | 65 |
| 85 | Peanut oil .. .. .. | Emulsion .. .. | 60 |
| 86 | Peanut oil hyd. .. .. | Dry .. .. | 80 |
| 87 | Peanut oil hyd. .. .. | Emulsion .. .. | 110 |
| 88 | Maize oil .. .. .. | Dry .. .. | 65 |
| 89 | Maize oil .. .. .. | Emulsion .. .. | 60 |
| 90 | Maize oil hyd. .. .. | Dry .. .. | 75 |
| 91 | Maize oil hyd. .. .. | Emulsion .. .. | 105 |

In all the loaves, with the exception of those containing unhydrogenated peanut and maize oils, the volumes ranged from good to very good. Peanut and maize oils, however, had a depressing effect upon volume although the colour was quite good. The loaves containing beef and mutton fats and unhydrogenated peanut and maize oils had an open but even texture and numbers 84 and 88 contained occasional cores. In the other loaves, the texture was fine, even, and soft. Beef and mutton suets and hydrogenated peanut oil produced loaves of average maturity, whilst unhydrogenated peanut and maize oils produced loaves which were definitely immature. Numbers 77, 81, and 91 were also of average maturity, numbers 76, 80, and 90 being slightly immature.

(ix) *Interface Modifying Ingredients*

In a dough containing added fat, small amounts of lecithin, or glycerol monostearate, are known to have a modifying effect on the interfaces between the particles of fat and the other dough constituents. It was thought that by adding a small amount of one of these substances to a dough into which fat had been mixed this interface modification might be sufficiently pronounced to produce a loaf equal to that produced when fat is added in the form of an emulsion.

In order to investigate this point, twelve baking tests were conducted on doughs containing 6 per cent. spray-dried skim milk powder, 2 per cent. lard, and small amounts of interface modifying ingredients. These ingredients were mixed with water before their addition. The results of the bakes are given in Table 12.

From the results of Table 12, it will be seen that the only bake in which the resultant loaf was superior to the control loaf was that in which 0·2 per cent. glycerol monostearate was added. Nevertheless, this loaf was still inferior to a loaf containing the same amount of fat in the form of an emulsion, the principal defect being a slight immaturity of the crust.

Because superglycerinated shortenings are not available in Australia, experiments with these fats could not be conducted.

TABLE 12.—THE ADDITION OF FAT AND AN INTERFACE MODIFYING CONSTITUENT TO BREAD

| Reference Number | Constituent | Amount | Bread Score |
|---|---|---|---|
| | | % | |
| Control | .. .. .. .. | .. | 100 |
| 92 | Egg lecithin .. .. | 0·0002 | 95 |
| 93 | Egg lecithin .. .. | 0·002 | 95 |
| 94 | Egg lecithin .. .. | 0·02 | 90 |
| 95 | Egg lecithin .. .. | 0·2 | 90 |
| 96 | Soya bean lecithin .. .. | 0·0002 | 95 |
| 97 | Soya bean lecithin .. .. | 0·002 | 95 |
| 98 | Soya bean lecithin .. .. | 0·02 | 90 |
| 99 | Soya bean lecithin .. .. | 0·2 | 95 |
| 100 | Glycerol monostearate .. | 0·0002 | 90 |
| 101 | Glycerol monostearate .. | 0·002 | 95 |
| 102 | Glycerol monostearate .. | 0·02 | 100 |
| 103 | Glycerol monostearate .. | 0·2 | 105 |

(x) *Skim Milk Powders Prepared as Egg Substitutes.*

Scientific and technical missions, sent by the Commonwealth Government to Germany, have included in their reports references to several whole egg and egg albumen substitutes which have been used with good results by German bakers. The production of these substitutes was fostered by the German Government about 1934 in its drive to discourage the importation of goods which required foreign currency. Several of the most popular substitutes, which contain considerable quantities of skim milk, are described hereunder.

"Milei V" is a whole egg substitute made in the following manner: Into 300 litres of skim milk are dissolved 600 grams of flaked sodium hydroxide, 600 grams of anhydrous sodium pyrophosphate, 600 cubic centimetres of egg yellow colour solution, and 6,000 grams of carub gum. This solution is then mixed with a further 700 litres of skim milk and the whole dried at once on a roller drying machine. The machine is fitted with steel rollers which take about 5 seconds for one complete revolution and which operate under a steam pressure of 7-8 atmospheres. The dried product is then sieved and packed. It has a colour similar to spray-dried whole egg powder but its texture and flavour resemble ordinary roller-dried milk powder.

"Milei W" is an egg albumen substitute prepared by mixing 5,200 litres of skim milk with 1,000 litres of whey and 23·2 kilograms of slaked lime. This is concentrated to a syrupy consistency and dried in a spray-drier in which the temperature of the ingoing air is 160°C.

and the outgoing air 70° C. The resultant powder is creamy-white in colour, of medium texture, and inclined to cake unless stored in airtight containers.

"Alroha Va," a whole egg substitute from Robert Pöhler of Hamburg, and "Synmilka," an egg albumen substitute from Schoppe and Schultz of Hamburg, are two other products manufactured from skim milk. The former, which contains 20-25 per cent. cereal starch, is a creamy powder with a rather coarse texture. The latter, which contains 10-15 per cent. added starch, is paler in colour and of a much finer texture. Manufacturing details are not available for either of these products.

Robert Pöhler has also marketed "Spar-Eipulver," an egg substitute in which only 50 per cent. of the powder consists of a skim milk substitute (probably "Alroha Va"), and "Trocken-Vollei," an unadulterated whole egg powder.

Samples of all these products have been obtained from Germany and used in test bakes on a 5 and 10 per cent. dry matter basis. The results of these bakes are given in Table 13.

TABLE 13.—THE ADDITION OF WHOLE EGG AND EGG ALBUMEN SUBSTITUTES TO BREAD

| Reference Number | Substitute | Amount | Bread Score |
|---|---|---|---|
| | | % | |
| Control | .. .. .. .. | .. | 100 |
| 104 | "Milei V" .. .. | 5 | 50 |
| 105 | "Milei V" .. .. | 10 | 60 |
| 106 | "Milei W" .. .. | 5 | 50 |
| 107 | "Milei W" .. .. | 10 | 30 |
| 108 | "Alroha Va" .. .. | 5 | 50 |
| 109 | "Alroha Va" .. .. | 10 | 40 |
| 110 | "Synmilka" .. .. | 5 | 45 |
| 111 | "Synmilka" .. .. | 10 | 40 |
| 112 | "Spar-Eipulver" .. | 5 | 50 |
| 113 | "Spar-Eipulver" .. | 10 | 40 |
| 114 | "Trocken-Vollei" .. | 5 | 80 |
| 115 | "Trocken-Vollei" .. | 10 | 70 |

When "Milei V" was added to doughs, the resultant loaves were immature, had a very small volume, and a slightly tough, close texture. "Milei W" also produced loaves which were immature and small in volume but in these loaves the texture was open and there were occasional cores. Both "Alroha Va" and "Synmilka" produced loaves which were immature, poor in volume, had tough textures and contained numerous cores. With "Spar-Eipulver," there was a slight improvement in maturity and volume but both loaves contained frequent cores. The best loaves were those containing "Trocken-Vollei." These loaves were only slightly immature and the volumes good. The loaf containing 5 per cent. "Trocken-Vollei" had a fine, even texture, but the texture of the other loaf was slightly coarse and open.

(xi) *Skim Milk Powders Containing Various Percentages of Fat*

A number of milk powders were next prepared by homogenizing various amounts of lard into fresh skim milk and spray-drying in a laboratory drier. Before adding the lard, the skim milk, which had an acidity of 0·18 per cent., was heated to 85°C. for 30 minutes. These powders were added to test doughs so that each dough contained 13 grams of powder but a different amount of lard. The results of these tests are given in Table 14. From these results it is seen that the optimum percentage of lard lies within the range of 21-28 per cent. Above 28 per cent. the value of the loaf decreased rapidly, owing principally to a reduction in volume and a slightly open crumb. Below 21 per cent., the value decreased slowly so that a loaf containing 14-21 per cent. lard was a decided improvement on an ordinary water loaf and only slightly inferior to loaves containing 21-28 per cent. lard.

TABLE 14.—THE ADDITION TO BREAD OF POWDERS CONTAINING DIFFERENT PERCENTAGES OF LARD

| Reference Number | Lard | Bread Score |
|---|---|---|
| | % | |
| Control .. .. .. | .. | 100 |
| 116 .. .. .. .. | 7 | 95 |
| 117 .. .. .. .. | 14 | 110 |
| 118 .. .. .. .. | 21 | 115 |
| 119 .. .. .. .. | 28 | 120 |
| 120 .. .. .. .. | 35 | 105 |

Because the addition of fat reduces the percentages of the various skim milk constituents, it is desirable not to add more fat than is absolutely necessary. It was therefore decided that 20 per cent., or slightly less, would be a convenient and effective amount of fat to incorporate in skim milk powders for future tests.

(xii) *Skim Milk Powders Containing Lard, Beef Fat, or Mutton Fat*

Arrangements were next made with a large milk-drying company for the manufacture of three special batches of skim milk powder. These powders contained approximately 19·6 per cent. mutton fat, beef fat, and lard respectively. Each batch was prepared from fresh skim milk, having an acidity of 0·16 per cent., and into which there had been mixed a percentage of fat equal to one-fourth the percentage of non-fatty milk solids. This mixture was preheated to 85°C. for 30 minutes and homogenized under a pressure of approximately 3,000 pounds per square inch. It was then condensed in a vacuum pan to one-third its original volume and dried in a Merrell-Soule spray-drier, the temperature of the drying chamber being approximately 76°C. and the time during which the powder was held at this temperature about 10 minutes.

These three powders were used in a number of baking tests, the results of these tests being given in Table 15. From these results it will be seen that there is no very marked difference between the baking properties of skin milk powders containing mutton fat, beef

fat, or lard. The powder containing mutton fat produced loaves with the best volume although the volumes of all loaves were good. The crumbs were fine, even, and soft. The powder containing lard produced a crumb with a particularly fine texture and this was largely responsible for the slightly higher scores of loaves containing this powder. All the loaves were of average maturity.

TABLE 15.—THE ADDITION OF VARIOUS AMOUNTS OF THREE SPECIAL POWDERS TO BREAD

| Reference Number | Fat in Powder | Amount of Powder | Bread Score |
|---|---|---|---|
| | | % | |
| Control | .. | .. | 100 |
| 121 | Mutton | 6 | 110 |
| 122 | Mutton | 8 | 115 |
| 123 | Mutton | 10 | 110 |
| 124 | Mutton | 12 | 110 |
| 125 | Beef | 6 | 110 |
| 126 | Beef | 8 | 110 |
| 127 | Beef | 10 | 115 |
| 128 | Beef | 12 | 115 |
| 129 | Lard | 6 | 110 |
| 130 | Lard | 8 | 115 |
| 131 | Lard | 10 | 120 |
| 132 | Lard | 12 | 115 |

In Australia mutton fat is less than half the price of ordinary skim milk powder and much cheaper than beef fat or lard. Hence, in future work, it was decided to use powder containing mutton fat in preference to beef fat or lard.

From the results of the preceding table, it will be observed that there is little difference in the physical properties of breads containing 6, 8, 10, and 12 per cent. powder. In a recent address Dr. F. W. Clements (1946) stated that in order to make a substantial contribution to the nutritional level of the Australian people, it would be necessary to add approximately 10 per cent. skim milk powder to bread. This would be equivalent to approximately 12½ per cent. of a powder containing 20 per cent. fat. It was at this level that it was decided to conduct further work on the development of a standard skim milk loaf.

### 3. Commercial Tests

Arrangements were made for the manufacture of another much larger quantity of skim milk powder containing slightly less than 20 per cent. mutton fat. The details of manufacture were similar to those already described. This powder was distributed to a number of commercial bakeries for the production of 2-lb. " tin " or " Devon " loaves, about 75 per cent. of the bread baked in Australia being of this type. The details of manufacture were left to the individual manufacturers, all of whom were very competent craftsmen. Some bakers gave the loaves a longer fermentation time, others preferred

to add extra yeast, and one baker added a small amount of cane sugar. For each pound of skim milk powder added, approximately 0·8 lb. of extra water was used.

(i) *Physical Properties of Commercial Loaves*

In general, loaves baked under commercial conditions were equal, and usually superior, to the ordinary water loaf produced in the same bakehouse. Where "high top" as well as "tin" loaves were manufactured, a small but definite increase in volume was noticeable. Also, the loaves containing skim milk powder were more symmetrical in shape.

In most bakeries, the skim milk loaves had a more pronounced colour, the crumb being quite creamy and the crust a dark straw colour. Some bakers thought this detracted from the value of the bread and they suggested that loaves containing such a high percentage of milk powder should be baked at a slightly lower temperature. The loaves were of average maturity and the textures of both the crust and crumb were good.

(ii) *Aroma and Palatability*

All the loaves containing skim milk powder were neutral in flavour and the layman found it difficult to differentiate between them and the ordinary control loaves. Nevertheless, most bakers were of the opinion that a better tasting loaf could be produced if beef fat or lard replaced the mutton fat.

Several bakers commented upon an unclean fatty odour which was given off during the baking process. This odour was scarcely noticeable in the finished loaves although it stresses the importance of utilizing only the highest quality fats in the manufacture of these special skim milk powders.

(iii) *Yield*

In previous experiments conducted at the William Angliss Food Trade School, West and Wilkinson (1946) added 3 per cent. skim milk powder to the dough mix. Neither the powder nor the remainder of the dough contained additional fat. This amount of powder increased the bread yield but the increase was not sufficiently great to offset the extra cost. For such a loaf to be profitable, therefore, it would have to be sold at a higher price. Although the present tests were conducted under totally different conditions, the conclusions arrived at are the same.

During the present investigation, several bakers costed their bakes and from the results of these costings it would appear that, when the milk powder was added on a 12½ per cent. dry matter basis, the extra yield obtained per bag of flour (150 pounds) was in the vicinity of 25 pounds of bread. This extra yield paid for little more than half the additional cost of adding milk powder. Hence, such loaves are economically possible only when they are sold at a slightly higher price.

## 4. Conclusions

Although the simultaneous addition of emulsified fat appears to overcome the major technical difficulty in the incorporation of skim milk powder in Australian bread, several problems still remain.

Because of an increased fermentation time, loaves containing 10 per cent. skim milk solids take approximately one hour longer to prepare. This can readily be overcome by adding cane sugar or additional yeast although a more satisfactory solution could probably be achieved by the introduction of a suitable lactose-fermenting yeast. During the latter part of this investigation, fat was very finely and evenly distributed throughout the dough mix by homogenizing it into the skim milk before converting it to powder. This was only one way in which satisfactory results could be attained. Commercially, it may be more desirable to add emulsified fat as a separate ingredient. Also, it has been apparent that the introduction of several small modifications in the baking technique would assist in producing a more satisfactory loaf.

In the near future, it is hoped to commence further work in which these problems will be investigated.

## 5. Acknowledgments

The authors wish to thank the American Dry Milk Institute in Chicago, Mr. N. E. Holmes of the Australian Scientific Research Liaison Office in London, and Mr. F. Galley of Queensland Cereal and Chemical Industries in Brisbane, for supplying samples of skim milk powders and flour, and Mr. J. R. Fisher of the New South Wales Department of Agriculture, and numerous commercial bakers for conducting independent baking tests.

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# An Electrolyte Resistance Thermometer for Measurement of Soil Temperature

*By C. G. Gurr, B.Sc.**

*Summary*

A resistance thermometer, using sodium chloride solution as the resistance element, has been found to have sufficient sensitivity for soil temperature to be measured with a standard commercial Wheatstone bridge.

Some means of measuring soil temperatures has been found desirable in connection with measurements being made of the water content of soils by an indirect method involving the measurement of the electrical resistance of gypsum blocks embedded in the soil. For convenience in field use it was desired to use the same Wheatstone bridge for both block resistance and temperature measurement. However, the bridge in use for the former did not have sufficient sensitivity for use with the usual metallic resistance thermometers.

Since the temperature coefficient of resistivity of electrolytes is so much greater than that of metals, being of the order of 2 per cent. per degree Centigrade, an electrolyte resistance thermometer was developed which on the same bridge measured temperature to an accuracy of approximately one quarter of a degree Centigrade. The greater accuracy of thermocouples and platinum wire resistance thermometers when used with appropriate measuring instruments is offset by the simplification of apparatus for the electrolyte resistance thermometers, where a high degree of accuracy is not necessary.

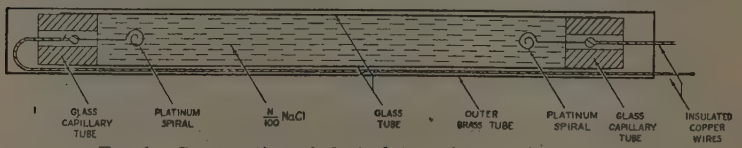


FIG. 1.—Construction of electrolyte resistance thermometer.

The form of the thermometer is shown in Fig. 1. The electrodes consist of platinum wire spirals fused onto copper leads which are cemented into short pieces of capillary tubing. The capillary tubes are in turn cemented into a four-inch length of glass tubing which contains the electrolyte. The whole is placed in a five-inch length of brass tubing for mechanical strength, and the ends sealed with wax.

The solution used was N/100 sodium chloride, which gave a resistance of the order of 20,000 ohms, falling in the most sensitive range of the bridge used. After manufacture the units required aging, since they increased in resistance at a given temperature until reaching a constant value in approximately ten days when the aging was done at 30°C.

* An officer of the Division of Soils.

At the low frequency (50 cycles per second) of alternating current used in the bridge, these thermometers have appreciable capacitance, which was balanced out to obtain the most sensitive resistance readings. Plotting resistance on a logarithmic scale against temperature as in Fig. 2 gave a straight line over the temperature range used, so that three points only were necessary for calibration of each thermometer over the range of 5°C. to 30°C.

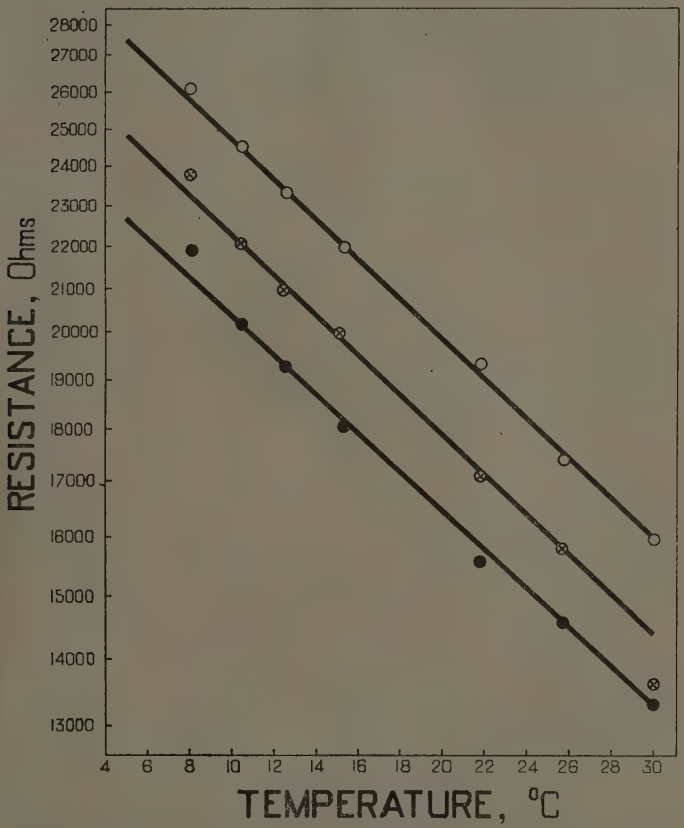


FIG. 2.—Calibration curves of three electrolyte resistance thermometers.

Owing to the high heat capacity of the thermometers there is a lag in response to temperature changes. At the depths of soil at which these units are being used, temperature changes are slow and the lag is not significant. For surface soils where temperature changes may be more rapid, this lag could introduce errors in temperature measurement.

Since these units were constructed, Bouyoucos (1947)* has published an account of a similar type of thermometer, using organic liquids as the resistance element, which can accommodate a much greater temperature range than the aqueous salt solution used above. The Bouyoucos units have other desirable features, such as platinum electrodes fused to the glass envelope, and small size, giving low heat capacity and hence less lag in response to temperature changes. These features should make the organic liquid thermometers more suitable for general use. However, for the soil conditions at present being examined, the thermometers developed in this laboratory have proved satisfactory.

* Bouyoucos, G. J. (1947).—New electrical resistance thermometer for soils. *Soil Sci.* 63: 291-8.

# The Water Absorption of Phenol-formaldehyde Resin Mouldings

*By R. P. Bowman,* J. S. Fitzgerald, M.Sc., Ph.D.,† and Florence M. Jensen, A.M.T.C.†*

*Summary*

Published work indicates that the absorption of water by plastics is a diffusion process involving two independent factors—the rate of penetration and the saturation limit. With phenolic mouldings in particular, the process is so slow that specimens of the size used in the standard water absorption tests are far from saturated after the normal immersion period. It is inferred that the standard tests give an approximate comparison of the rates of penetration of water into various plastics, provided they do not differ greatly in their saturation level.

It is shown that water absorption by moulded phenolics conforms to the diffusion equation with an accuracy that depends on the filler used. Thin specimens may be used to obtain a measure of the saturation limit of mouldings, but the total percentage of water absorbed varies with the thickness of the specimens.

In the standard B.S.S. and A.S.T.M. tests the results are sensitive to the moisture content of the moulding powders and to the treatment of moulded specimens before conditioning.

It is concluded that for satisfactory comparison of plastics the rate of penetration of water and the saturation value must both be measured. However, if the present standard type of test is retained, more details should be specified than are given in either B.S.S. 771 or A.S.T.M. D570, particularly with regard to the moisture content of the powder before moulding, and treatment of specimens. The A.S.T.M. procedure is preferred to the B.S.S., but results should be expressed as a rate of penetration.

## 1. Introduction

In Australia the physical, mechanical, or electrical properties of plastics are determined according to methods developed either by British or American testing authorities. During the war there has been an increasing use of British Standard Specifications, particularly by the Services, while manufacturers have used both British and American methods in controlling the quality of their products.

Now that the establishment of Australian standards for some plastics is under consideration, it is necessary to examine critically the existing methods of test. German procedures should be taken into account as well as British and American, though there has been far less experience of them in Australia. Each test procedure will need separate consideration, for it is only to be expected that differing methods will each contain desirable features. Moreover there is some confusion in the application of standard tests, largely due to differences in their purpose. Test methods of the British Standards Institution have usually been developed for a particular type of material, whereas those of the American Society for Testing Materials are applied to a wide range of plastics. The result is that some British books on plastics describe the British tests for certain properties, but in comparing different materials they list results found, apparently, by the American methods (1, 2).

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† An officer of the Division of Industrial Chemistry.

If other than an arbitrary choice of method is to be made, a review of available literature supplemented by a certain amount of experimental work will be needed in connexion with each test examined. The present paper deals with the measurement of water absorption of moulded materials, particularly moulded phenol-formaldehyde resins, examining the standard British and American tests in the light of published work and further experimental data.

## 2. Previous Work on Water Absorption

(i) *The Factors Involved*

A considerable amount of work has been directed to the study of the penetration of water into solids, and the theoretical aspects of the diffusion process have been thoroughly examined (3). Possibly the best discussion of the subject as it applies to plastics is that given by Irany (4) based largely on his experiments with various polyvinyl plastics. He describes the two types of absorption, diffusion, and capillary penetration. The latter type may be represented by equation (A) which gives a parabolic curve, implying a breakdown of the material before reaching saturation.

$$W = C\sqrt{t} \quad \ldots\ldots\ldots (A)$$

where $W$ is the total absorption per unit area at time $t$ and $C$ is a material factor.

For absorption when the rate is governed by diffusion Andrews and Johnston (5) and later, but independently, Irany (loc. cit.) developed similar expressions from Fick's law, which showed that the amount of water entering a solid was dependent on two factors, the rate of penetration and the saturation limit.

When the solid considered is in the form of a sheet, the expressions from both papers may be written as equation (B).

$$\frac{W}{S} = 1 - \frac{8}{\pi^2}\left(e^{-Kt} + \frac{1}{9}e^{-9Kt} + \frac{1}{25}e^{-25Kt} + --\right) \ldots\ldots (B)$$

when $K = \dfrac{k\pi^2}{d^2}$ (Andrews and Johnston) or $= \dfrac{P}{d^2}$ (Irany),

$d$ is the thickness of sheet,

$W$ is the total water absorption per unit area at time $t$,

$S$ is a constant depending on the saturation limit of the material under the conditions of the test,

$K$, $P$, $k$ are constants depending on the permeability of the material.

The absorption of water by most homogeneous resins accords with equation (B), and hence follows the diffusion law. Andrews and Johnston (5) showed this held approximately for rubber, and later Leopold and Johnston (6) found it held accurately for "clear Bakelite." Irany (4) showed that diffusion was the governing principle in absorption by various polyvinyl acetates and acetals, but when these contained a filler the absorption rates followed the capillarity equation (A), even though the filler was a non-absorbent mineral powder. He also showed that the same equation held for a laminated Bakelite which contained a fibrous filler. Though Taylor (7) reported phenolic

resins and vulcanized rubber as reaching equilibrium (saturation), he found that in most cases water absorption followed the capillary law up to a point since the water absorbed increased as the square root of the time. Some of the results given by Kline, Martin, and Crouse (8) were used by Irany as examples of diffusion (see Table 2 later), but for the cast phenolic resin the original figures, with the exception of the final two measurements, fit a single constant parabolic curve as well as they do the curve drawn from Irany's two constants.

A number of workers who have studied water absorption of various plastics, including materials containing fillers, have stressed that two factors are involved, saturation level and permeability. It is therefore of interest to examine the literature in which these factors have been distinguished, and to find what methods have been used to discriminate between them, and what significance has been placed on them. This is particularly necessary since both the British and the American standard test methods lead to but one numerical value as a measure of absorption.

(*a*) *Rate of penetration.*—Irany used 4 in. by 1 in. specimens of various thicknesses sealed at the edges, which were soaked for prolonged periods, removed and weighed at intervals. To measure saturation, very thin specimens were used, of the order of 0·4 mm. thickness, while specimens for the measurement of the rate of absorption were approximately 2 mm. thick.

In most cases of practical interest the rate of penetration is slow, and most of the water remains near the surface unless the exposure is sufficiently prolonged. Irany therefore concluded that experiments based on such short immersions as that accepted by the A.S.T.M., namely 24 hours at 25°C. for a specimen 0·125 in. thick, yield comparative rate values but no information on absorption capacity. The scope of A.S.T.M. method D570-42 (9) is specifically limited in its first section to "the procedure for determining the relative rate of absorption of water." However, Note 2, later in the same section, causes confusion when it states that the test is "a guide to the proportion of water absorbed by a material——."

The water absorption test of B.S.S. 771 (10) specifies a thicker disc, approximately 0·4 in., and 7 days' immersion at about 20°C. It is not stated that only the rate of absorption is indicated and not the saturation limit. Test pieces of the same thickness as the B.S.S. specimens were used by Pinten (11), who soaked mouldings 100 mm. by 15 mm. by 10 mm. in size. He recognized that it is not possible to obtain a complete and reliable evaluation of water absorption on the basis of tests for such short periods as 7 days, for this, he said, gives only a velocity characteristic of the material, whereas saturation value is also important. Nevertheless he classified plastics according to their absorption in this period.

Kline, after a more general paper which summarized existing tests (12), published with Martin and Crouse (8) what is probably the most comprehensive work on water absorption. This paper provided the experimental basis for the present A.S.T.M. test. Using a selection of thermosetting and thermoplastic materials, these workers investigated water absorption during short and long immersions as well as the effects of conditioning the moulding in several ways. Their

results do not point to any one set of conditions as outstandingly suitable for a test. Even with those adopted by A.S.T.M. and incorporated in test D570-42, certain limitations must be borne in mind in interpreting the results.

From prolonged immersion tests Kline showed that for most of the materials maximum absorption was not reached until about 16 weeks or longer, though cellulose acetate and nitrate reached a maximum in under 8 weeks, possibly in one week. It is obvious that immersion for 24 hours, the time adopted for the A.S.T.M. test, measures only the initial rate of absorption and has no direct relation to saturation value; indeed the relative order of materials may be entirely altered by changing from one basis to the other, as is shown by the following extract from Kline's results.

TABLE 1.—WATER ABSORPTIONS (Kline, 8)

| Material | Percentage Gain during Immersion | |
|---|---|---|
| | 24 Hours | 100 Weeks |
| Phenolic cast .. .. .. .. | 0·24 | 7·0 |
| Methyl methacrylate .. .. .. | 0·33 | 1·5 |
| Phenolic moulded .. .. .. .. | 0·34 | 6·8 |
| Urea moulded .. .. .. .. | 0·75 | 5·2 |
| Ethyl cellulose .. .. .. .. | 0·83 | 4·0 |
| Cellulose nitrate .. .. .. .. | 0·98 | (2·1)* |
| Polyvinyl butyral .. .. .. .. | 1·07 | 9·8 |
| Cellulose acetate .. .. .. .. | 2·5 | (5·2)* |

* Seven days' immersion (maximum value recorded).

Too few data were given by Kline, Martin, and Crouse to permit the saturation values to be calculated for cellulose nitrate or acetate since plasticizer loss between one and eight weeks exceeded any gain in water. The fractional saturation reached in 24 hours by these materials and by a moulded phenolic shows, as an extreme example, that an arbitrary choice of time gives no comparable basis for different plastics. Lawton and Nason (13) gave water absorption figures for cellulose acetate and cellulose nitrate specimens 0·125 in. thick and less, which showed saturation values of 8 and 2·5 per cent. by weight respectively. In the first 24 hours' immersion the two materials took up 2·08 and 0·98 per cent. water, that is, 25 and 40 per cent. of their total absorption. Figures in Table 1 show the phenolic moulding absorbed only 0·34 per cent. water in the first 24 hours, that is, 5 per cent. of its saturation capacity, which was 6·8 per cent. of its weight. Comparison of the different materials if made on the results of 24-hr. immersion, would be influenced more by rates of absorption than by saturation values, but would give a true picture of neither.

Some of Kline's figures were examined by Irany, who derived the constants shown in Table 2 for his diffusion equation (B).

TABLE 2.—CONSTANTS FOR DIFFUSION* (Irany, 4)

| Material | *S* (Saturation) | *P* (Permeability) |
|---|---|---|
| | Vol. % | Sq.cm./day |
| Methyl methacrylate .. .. .. | 1·5 | 0·0023 |
| Phenolic cast .. .. .. .. | 8·6 | 0·0002 |
| Polyvinyl butyral .. .. .. | 10·3 | 0·0003 |

* These constants give only poor agreement with the original figures.

These figures emphasize the conclusion implicit in Kline's work, that saturation and permeability place materials in very different relative positions. They indicate, moreover, that the 24-hr. absorption does not correspond to the permeability constant in Irany's equation. Sufficient figures from strictly comparable materials are not available to make detailed comparisons, but Irany's permeability coefficients would place materials in substantially the same order as constants found for the diffusion of water vapour through plastics.

(*b*) *Saturation value.*—From the literature it would seem that the existing type of test gives an approximation to the rate of water absorption, which satisfies the practical requirements of a specification limited to similar plastics. Moreover, it would at first appear that the saturation value, reached only after very prolonged immersion, is mainly of theoretical interest. The effects of the two factors, permeability, and saturation value, are described as follows by Irany:—"A high saturation limit, *S*, indicates a high water concentration in the exposed surface and, eventually, deleterious effects in such applications which depend mostly on the permanence of the surface (for example in protective coatings). On the other hand, a high rate of penetration, *P*, would not necessarily affect the surface, but would favour the rapid admission of water to the interior of more bulky objects and cause changes in shape, dimensions, strength, dielectric, or other vital properties." Support is therefore given to the present standard type of test for most applications. However, the necessity for a means of measuring saturation value is shown by such papers as those of Mellon (14) and of Gordon, Brown, and McGrory (15), who considered that for protein plastics only the saturation value was of use. Mellon obtained his measurements in a relatively short time by reducing the thickness of the A.S.T.M. specimen to 1/16 inch, and he noted from a few tests that the method might be suitable for cellulose acetate, urea—and melamine—formaldehyde resins, but not for phenolics.

A method which could be used for measuring saturation absorption is indicated by Shearman and co-workers (16). Adopting a new approach to the problem, they attempted to evolve tests for specimens cut from moulded articles, instead of using specially moulded test pieces. Miniature specimens were tested, and for water absorption, filings were also used. For the absorption tests, specimens 20 mm. by

10 mm. by 0·15 mm. were cut as shavings and immersed for 14 days. In general, materials were placed in the same order as by the standard B.S.S. test if results were expressed as absorption per unit area—a finding which seems anomalous, for one would have expected such thin shavings to have reached saturation. However, comparison of absorptions on a weight basis for small specimens immersed in water and for filings exposed to high humidity, gives some interesting results. The figures given in Table 3 have been taken from the report as an illustration, and it is obvious that the effects both of permeability and saturation are involved.

TABLE 3.—WATER ABSORPTIONS (Shearman, 16)

| Material.* | In Water | | In Air at 100 Per cent. R.H. |
|---|---|---|---|
| | Standard | Small | Filings |
| | Mg./sq.cm. | Mg./100 mg. | Mg./100 mg. |
| Phenolic, wood-flour filled .. | 3·24 | 1·74 | 15·1 |
| Phenolic, shock-resistant .. | 6·70 | 6·26 | 12·65 |
| Urea, moulded .. .. | 9·42 | 9·55 | 16·2 |

* A description of the materials has been given in preference to the trade numbers used by Shearman.

Though Shearman and his co-workers do not clearly distinguish between rate of penetration of water and saturation value, the two are obviously of differing importance in the various methods used. From their results the authors conclude that the filings method gives values characteristic of the material rather than of the moulding, since the features of the moulding mainly effective in preventing penetration of moisture have been destroyed by the reduction to powder. They state that both the filings method and that involving immersion of specimens will need to be used if full information regarding both moulding and material is required. It would be better, in our opinion, to interpret the results in terms of saturation and permeability. The differences found depend primarily on surface area and not on other characteristics of the moulded article as distinct from those of the material itself.

Measurements of absorption in atmospheres of high relative humidity were compared by Zebrowski (17) with water absorptions obtained by immersion. He showed that phenolic mouldings exposed to a saturated atmosphere for a period of four years, absorbed water more slowly than by immersion, but ultimately attained a similar value.

Thus two methods have been proposed for obtaining the saturation limits of water absorption: exposure of filings to atmospheres of high relative humidity, and immersion of thin specimens. The work of Shearman throws doubt on the validity of this second method, but we will discuss it later in conjunction with some of our own results.

(ii) *The Standard Tests*

Assuming, now, that the short time immersion test with moderately thick specimens gives the comparative rates of absorption of water with sufficient accuracy for limited comparisons, it has yet to be ascertained whether the standard tests as described in A.S.T.M. and B.S.S. specifications are sufficiently defined. The details of the tests are set out in the experimental section of this paper, and in what follows certain aspects will be discussed in the light of published information. It is realized that there must be much information in the files of testing laboratories in America and England, but so far as we know this has not been collated.

(*a*) *Expression of results.*—We have concluded above that the standard type of test measures a rate of absorption, and it follows that this would be more explicit if the test results were expressed as a rate. This is of importance since test results are often referred to by users of plastics who have little knowledge of the details of the specifications. B.S.S. water absorption results are reported as the weight of water absorbed. This implies an arbitrary standardization of specimen size, but does not sufficiently emphasize the importance of time. For the A.S.T.M. test, absorption is expressed as a percentage of the specimen weight. This is still less informative; it places the emphasis on weight of specimen rather than on area, and emphasizes the importance neither of specimen size nor of time. The adoption of this mode of expressing results is rather surprising, for it seemed that Kline, Martin, and Crouse (8) had accepted the assumption that absorption per unit area placed materials in their correct relative order, though admittedly they expressed most of their results on a weight percentage basis. Certainly with specimens of constant size the errors caused by using a weight percentage will be of a minor character: they arise from differences in the density of various plastics. The use of the method by Kline, Martin, and Crouse cannot be justified even this way, for they used thicknesses ranging from 0·121 to 0·185 in., giving specimens varying by 6 per cent. at most in area, but in weight up to 40 per cent.

(*b*) *Removal of moulded surface.*—With regard to differences in the experimental technique of the A.S.T.M. and B.S.S. methods, the most obvious is the machining of the specimen for the latter test. There is little published information on this, though the intention seems to be to avoid dependence on surface finish and to simulate worst service conditions. Azam and Luce (18) published a few results for tests on fabric-filled phenolic mouldings which undoubtedly show a greater absorption by sanded specimens than by untreated ones. Their conclusion that full cure reduces the difference between the two types of specimens is not fully supported by their results.

A more satisfactory treatment of this subject is published in a report by the British Electrical and Allied Industries Research Association (19). Their results indicate that specimens with the surface removed by grinding have an increased water absorption, particularly if fabric-filled. The tests were based on B.S.S. 771, but went beyond its usual limit by including polystyrene and thermosetting resins other than phenolics, and also by prolonging the soaking period up to 72 days. It was concluded that the value obtained in the usual short-time test is likely to be a closer approach to the final (saturation)

value if the skin is removed from a moulding than if the skin is retained. This is certainly true, but it can only be of quantitative significance if the values obtained in the short time are of the same order as the saturation values. Results given later in the present paper show this is far from being the case for B.S.S. discs, and in the report cited insufficient time was allowed for saturation to be approached.

(*c*) *Conditioning of powder and specimen.*—Conditioning of test pieces, before immersion in water, is required by both A.S.T.M. and B.S. specifications, and the merits of the conditioning periods specified will be discussed later. In neither specification are limits placed on the treatment of specimens between moulding and conditioning, nor is any attempt made to ensure that moulding powders are in a standard state before moulding. It is generally recognized that the moisture content of the powder influences the water absorption of the moulding; however, few figures are available, probably because knowledge of how to obtain the best article from a powder has been regarded as part of a successful moulder's art. In two reports by Barwell and Pepper (20) are details of the water absorptions for laminated paper impregnated with a phenolic resin, and dried to different degrees before pressing. There was a very marked decrease in water absorption with increased drying before moulding, but the authors pointed out that " The results obtained after even 7 days' immersion in water are not saturation values and may be interpreted only as evidence of the rate of water absorption."

Recent interest in high-frequency pre-heating of moulding powders has focused attention on the treatment before moulding. Dring (21) has shown that under the conditions of B.S.S. 771, but using specimens moulded after high-frequency pre-heating, there is a decrease in water absorption as compared with normal mouldings, from 107 mg. to 80 mg. for a good wood-flour filled phenolic powder, and from 147 mg. to 101 mg. for a xylenol resin with wood-flour filler. It is possible that the effect on water absorption is wholly due to the drying of the powder, though undoubtedly this method of pre-heating allows a thoroughly hot powder to be used in the mould, with consequent improvement in flow and reduction in curing time. With regard to a closely allied subject, it is of interest to note the graph given by Pinten (11), which shows that post-stoving of specimens (24 hours at 150°C.) not only decreases the rate of absorption but also lowers the saturation value.

(*d*) *Moisture content of powder.*—It is usually assumed that the powder as received is the material to be tested. However, samples are not always kept in airtight containers, and it may be desirable to condition them to a standard low humidity before moulding. If so, the moisture content of the powder before and after conditioning should be determined. No standard procedures have been suggested for determining the moisture content of thermosetting moulding powders. Cornish (22) states that work in the laboratories of Messrs. Halex Ltd. has shown that most methods suggested for determining the moisture content of moulding powders are unreliable. He used the Karl Fischer reagent and obtained satisfactory results with several types of powders. His procedure should serve as a useful guide in the preparation of a standard test.

## 3. Experimental

The published work just reviewed is insufficient for comparison of B.S.S. and A.S.T.M. methods of determining water absorption, and for deciding whether such factors as moisture content of the moulding powder or storage of specimens after moulding, at present not mentioned, should be delimited. The evidence regarding the usefulness of thin specimens for determining saturation values is conflicting. The tests described in the following sections provide some further information to assist in formulating a standard test, and indicate lines for further work should it be considered desirable to measure the absorption at saturation.

(i) *Materials Used*

The moulding powders used in the preparation of the test pieces were all commercial products of Australian firms except Nos. "E" and "F" which were imported. Some details of their composition are given in Table 4. The approximate impact strengths (B.S.S. Izod) are also given, since water absorption is often taken to a limited extent as varying in the same way as impact strength, though not proportionately. The moisture content of the powder as measured immediately before moulding specimens is also given in this table, though for some tests made at different times other values were found and are quoted with the relevant experiment.

TABLE 4.—POWDERS USED AND THEIR MOISTURE CONTENTS.

| Ref. No. | Type* and Filler | Filler | Resin Type | Izod. | Moisture Content | |
|---|---|---|---|---|---|---|
| | | | | | Normal | Dried |
| | | % | | ft./lb. | % | % |
| A | GX Wood-flour .. | 42 | 2 Stage | 0·27 | 4·2 | 1·8 |
| B | HS Macerated Fabric .. | 44 | 2 Stage | 0·9 | 6·3 | 3·8 |
| C | MS Mixed Wood and Fabric | 46 | 1 Stage | 0·4 | 5·5 | .. |
| D | Mica .. .. .. | 68 | 2 Stage | 0·12 | .. | 1·2 |
| E | GX Wood-flour .. | .. | .. | .. | 5·3 | 1·95 |
| F | HS Canvas .. .. | .. | .. | (1.0) | 5·6 | 2·4 |
| G | GX Wood-flour .. | 42 | 2 Stage | .. | .. | .. |
| H | G Wood-flour .. .. | 42 | 2 Stage | .. | 4·6 | .. |
| J | Expl. Wood-flour .. | 25 | 1 Stage | 0·18 | 4·0 | 1·3 |

* According to B.S.S. 771.

(ii) *The Standard Methods*

German methods for testing moulded plastic materials need not be discussed here for Specification DIN 7701 (23) includes only a qualitative test, namely, immersion for 15 minutes in boiling water, a process which should bring about no significant change.

Quantitative methods are set out in British Standard Specification (B.S.S.) 771-1938 (10) and in D570-42 (9) of the American Society for Testing Materials (A.S.T.M.). Essentially the two tests are similar: they involve moulding a disc, immersing it in water for a given period, drying and determining the increase in weight. Briefly the details which apply to moulded phenolic materials are as follows:

B.S.S. 771-1938, Appendix E.

A disc 50 $\pm$ 1 mm. (1·97 $\pm$ 0·039 in.) diameter, 12 $\pm$ 1 mm. (0·47 $\pm$ 0·039 in.) thick, is moulded in a positive type mould under specified conditions of pressure, temperature, and time; cooling in the mould under pressure is allowable, which varies the last two conditions. The skin is removed by machining, leaving a disc 48 $\pm$ 0·2 mm. (1·89 $\pm$ 0·008 in.) diameter 10 $\pm$ 0·2 mm. (0·394 $\pm$ 0·008 in.) thick. This is conditioned for 1 hour at 50°C. cooled in a desiccator, weighed, immersed in water at 20°C $\pm$ 5° for 7 days, wiped dry, air-dried for 5-15 mins. and weighed. Water absorption is expressed as mg. increase in weight.

A.S.T.M. D570-42.

A disc 2 in. diameter, 0·125 $\pm$ 0·007 in. thick, is moulded, suitably in the type of mould detailed in method D647-42T (24), which shows a fully positive mould in which the chase is only 0·020 in. higher than the two forces together. No conditions are given for making the moulding though the 2 in. disc will ultimately be included in D796-44T on moulding practice (25). The disc as moulded is conditioned for 24 hours at 50°C. $\pm$ 3° or for 1 hour at 105-110°C. if comparison with other plastics not required. It is cooled in a desiccator, weighed, immersed in water at 25°C. $\pm$ 2° for either 2 hours or 24 hours (the latter usually for phenolic mouldings), wiped dry and weighed immediately. The weight increase, expressed as a percentage of the weight of the conditioned specimen, is taken as the water absorption.

It is of interest to note that in the forerunner of this test, D48-39, a 4 in. disc $\frac{1}{8}$ in. thick was used. All materials not affected by such temperatures were conditioned for 24 hours at 100°C. $\pm$ 5°, and 48 hours' immersion at 25°C. $\pm$ 2° was required.

(iii) *Methods Used*

Water absorption determinations were made by the B.S.S. and A.S.T.M. methods. A fully positive mould was used, giving a disc 2 in. diameter. The weight of charge was adjusted to give 0·45 in. thickness for B.S.S. specimens and 0·125 in. thickness for A.S.T.M. To minimize the possible effects of storage before conditioning a strict time schedule was observed. A.S.T.M. discs were placed in the conditioning oven the day after moulding and immersed the next day. B.S.S. discs were machined the day after moulding and conditioned and immersed the next day. Most experiments were done in duplicate but for the long-term soaking and some other tests five specimens were used for each set. The moulding schedule was arranged so that as many treatments as possible were covered each day, and replicates were moulded on different days. Powders were moulded at 3,000-4,000 lb./sq.in. and 160°C. $\pm$ 5°, the B.S.S. specimens for 15 mins., the thinner A.S.T.M. ones for 6 mins., except where otherwise stated.

After immersion and before weighing, specimens were wiped rapidly with damp and with dry cloths, left on a three-point suspension under a crystallizing dish to dry in still air for 5 minutes and then weighed. Discs immersed at 50°C. were left 15-45 mins. in water at 25°C. before weighing. Immersion was normally in distilled water at 25°C. $\pm$ 1°, specimens being held on edge in slots cut in a bent piece of methyl methacrylate sheet.

Moisture contents of powders were determined by heating 2-4 g. samples at 100°C. for 24 hours, using shallow aluminium dishes covered by lids during the cooling and weighing. Dishes were cooled on a metal block in a desiccator for 10 mins. and weighed immediately.

(iv) *Drying Wet Specimens before Weighing*

The difference between the details given in the A.S.T.M. and B.S. specifications concerning the drying of the discs after soaking and before weighing probably originated because of the rougher surface of the machined discs in comparison with the smooth mould finish. A.S.T.M. procedure is to remove the surface water with a dry cloth and weigh immediately, whereas B.S.S. specify a thorough drying by pressing with blotting paper, followed by more than 5 but less than 15 minutes' drying in still air at 15-25°C.

Materials that gave a range of water absorptions were tested. Discs were weighed at intervals after wiping with a towel. Machined discs required 5 minutes' air-drying before they appeared superficially dry. Results were slightly erratic as might be expected from the nature of the experiment, but the loss during drying varied with the water absorption. The results set out in Table 5 are grouped according to the range of water absorption, and are sufficiently accurate only to show the order of the error.

TABLE 5.—DRYING OF DISCS BEFORE WEIGHING

| Disc. | Absorption | Drying Error in Interval | | |
|---|---|---|---|---|
| | | 1–4 Mins. | 1–11 Mins. | 1–20 Mins. |
| | mg. | mg. | mg. | mg. |
| A.S.T.M. .. .. | 2–15 | 0·1 | 0·2 | 0·3 |
| „ .. .. | 40–140 | 0·3 | 1·5 | 3·0 |
| | | 5–10 Mins. | 5–15 Mins. | 5–30 Mins. |
| | | mg. | mg. | mg. |
| B.S.S. .. .. | 100–120 | 2·0 | 3·5 | 6·0 |
| „ .. .. | 150–200 | 4·0 | 6·0 | 9·0 |

(v) *Absorption during Prolonged Immersion*

A test was made to find the effect of prolonged immersion on the water absorption of different types of phenolic mouldings.

Materials A-D (Table 4) were used. Conditioning for both B.S.S. and A.S.T.M. size of specimens was 24 hours at 50°C. Five specimens were used for each series of measurements. Owing to the numbers involved, up to a week was allowed between moulding and setting up. Immersion was at 25° and 50°C. and specimens were replaced in water after each measurement. With the prolonged immersion of many specimens, particularly at the higher temperature, it was thought preferable to change the water every few weeks. In the later stages the 50° specimens were placed in water in a 1-gallon bottle with a screw lid, and left in an oven. A strong smell of naphthalene developed and the solution became slightly alkaline. No allowance was made for any material extracted by the water.

Most of the results are represented in Figs. 1-3, though some of the points for short-time immersion have been omitted to simplify the figures. In general, the results are of the type expected, with

the absorptions in 24 hours or 7 days only a small proportion of the saturation value, and with the thicker specimens absorbing a greater total weight of water.

The shape of most of the curves points to diffusion being the governing process and this has been confirmed by finding close agreement with a theoretical curve in some cases, and approximate agreement in others. The results did not fit the capillary absorption equation (A) given earlier, and moreover this equation makes no allowance for attainment of a saturation limit. For expressing the results according to equation (B), all its terms after the first may be neglected for values of $Kt$ greater than about 0·25, when $W/S$ is over 0·37. The expression then reduces to the form (C) in which it was used by Irany. It can also be written as shown in (D), the form used by Andrews and Johnston.

$$W = S\left(1 - \frac{8}{\pi^2} \cdot e^{-Kt}\right) \qquad \ldots\ldots\ldots\ldots \text{(C)}$$

$$Kt = -\ln\left(1{\cdot}234\left(1 - \frac{W}{S}\right)\right) \qquad \ldots\ldots\ldots\ldots \text{(D)}$$

In using this equation we chose a suitable value for $S$ after graphing the results. Observed values of $W$ were neglected when $W/S$ was below 0·37 (since the simplified equation does not then hold), and also when $W$ was nearly equal to $S$ (since small deviations are unduly magnified). Values for the remaining points, expressed as in (D), were then averaged. Division gave $K$, the permeability constant for the thickness of specimen under consideration, values for which are shown in Table 6. The derived curves are drawn as full lines in Figs. 1-4.

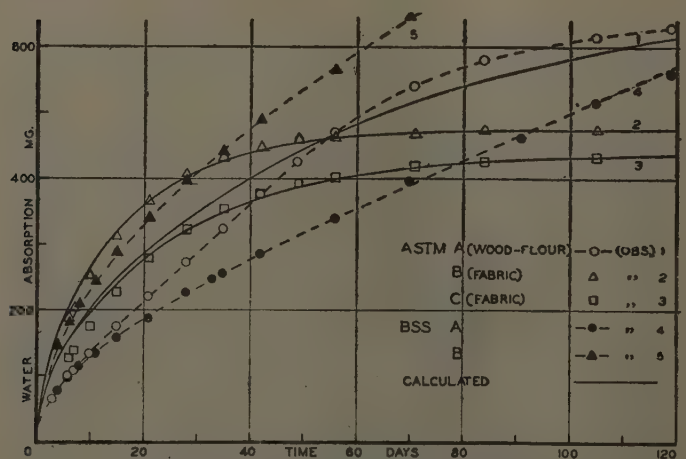


FIG. 1.—Specimens immersed at 25°C.

TABLE 6.—DIFFUSION CONSTANTS (EQUATION B) FOR ABSORPTION.

| Powder | Test | Temp | Agreement with Observations | $S$. | $K$. | $P = Kd^2$ |
|---|---|---|---|---|---|---|
| | | °C. | | % | 1/day | sq. in./day |
| A .. | Min. .. | 25 | Good .. | 5·30 | 0·56 | 0·00085 |
| | „ .. | 50 | Good .. | 5·60 | 2·11 | 0·0032 |
| | | | | mg. | | |
| | A.S.T.M. .. | 25 | Poor .. | 700 | 0·016* | 0·00025* |
| | „ .. | 50 | Poor .. | 700 | 0·10* | 0·0016* |
| A dried .. | „ .. | 50 | Poor .. | 925 | 0·065* | 0·0010* |
| „ .. | B.S.S. .. | 25 | Saturation not approached | | | |
| „ .. | „ .. | 50 | Poor .. | 2,260 | 0·016* | 0·0024* |
| | | | | % | | |
| B .. | Min. .. | 25 | Good .. | 4·35 | 0·87 | 0·0013 |
| | „ .. | 50 | Good .. | 4·35 | 2·50 | 0·0038 |
| | | | | mg. | | |
| | A.S.T.M. .. | 25 | Good .. | 475 | 0·060 | 0·00093 |
| | „ .. | 50 | Good .. | 475 | 0·20 | 0·0031 |
| B dried .. | „ .. | 50 | Good .. | 625 | 0·12 | 0·0019 |
| „ .. | B.S.S. .. | 25 | Saturation not approached | | | |
| „ .. | „ .. | 50 | Fair .. | 1,750 | 0·019 | 0·0030 |
| C .. | A.S.T.M. .. | 25 | Fair .. | 440 | 0·039 | 0·00061 |
| | „ .. | 50 | Good .. | 490 | 0·175 | 0·0027 |
| D dried .. | „ .. | 25 | Saturation not approached | | | |
| „ .. | „ .. | 50 | Poor .. | 300 | 0·0088* | 0·00014* |
| J .. | „ .. | 50 | Good .. | 800 | 0·125 | 0·00195 |
| J dried .. | „ .. | 50 | Good .. | 1,100 | 0·105 | 0·00165 |

* Where the curve calculated from these constants agrees only poorly with the points observed, the constants must be taken as approximations only. For comparison of the curves see Figs. 1-4.

Good agreement between experimental results and the requirements of the diffusion equation was not obtained in all instances, and was particularly poor for the wood-flour filled powder. For this material, the graph of results expressed as in equation (D) gave a flat sigmoid curve which approximated to a straight line through the origin. From the graph of absorption against time, it can be seen that, for a considerable portion of the process, absorption by the wood-flour filled mouldings is directly proportional to time.

The deviations from the theoretical shape of curve are small enough to warrant the assumption that diffusion is the main process involved, but that the postulates made in deriving the equation are not all fulfilled. Some capillary action would be expected with the cellulosic filler, but this should be greatest with the fabric filler which nevertheless gave the best agreement with the diffusion equation.

The saturation values were usually similar at 25° and 50°: this was confirmed by using miniature specimens (see Section 3 (vi)). With the wood-flour filled mouldings the higher temperature caused an increased absorption in some instances. The total absorption (saturation absorption) on a weight percentage basis was higher with the larger specimens. For the B.S.S., A.S.T.M. and miniature specimens respectively, 9·4, 8·0, and 5·5 per cent. were found for the

wood-flour and 7·2, 5·4, and 4·4 per cent. for the fabric-filled material. There appears to be no simple explanation for this but it must be kept in mind in formulating a test.

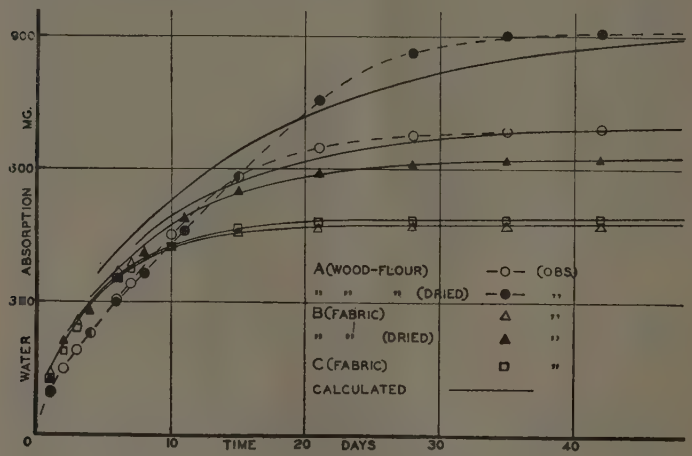


FIG. 2.—A.S.T.M. specimens immersed at 50°C.

In Section 3 (vii) of this paper, figures will be given showing the decrease in water absorption, as measured by the conventional tests, caused by drying the moulding powder before making the test piece. The constants listed in Table 6 indicate that, in the present test, mouldings from pre-dried powders had a lower permeability than those from powders of higher moisture content, but that at saturation they had absorbed a greater amount of water. This difference in saturation absorption may merely reflect the initial difference in moisture content and indicate that at saturation a moulding has a constant water content irrespective of the moisture content of the powder from which it was made. Pre-drying of powders "A," "B," and "J" caused moisture losses of 230, 230, and 240 mg. respectively, while mouldings from the dried and normal powders differed in total absorption by 225, 250, and 300 mg. for the powders mentioned. The significance of this approximate correspondence has not yet been determined.

The reversal of the relative order of different types of moulding materials when compared at saturation and not, as is usual, in the initial stages of absorption, is clearly shown in Figs. 1, 2, and 3 where the curves for materials "A" and "B" cross after 50 days' soaking for A.S.T.M. discs at 25°C., and after a similar period for the B.S.S. size of discs at 50°C.

Comparison of results obtained with the two sizes of specimen is only valid for the pre-heated powders, all the present B.S.S. specimens having been made with them. Figures for the initial absorptions at 50°C. are given in Table 7.

TABLE 7.—WATER ABSORPTIONS OF B.S.S. AND A.S.T.M. DISCS

| Time. | Water Absorption (mg. per disc) at 50° C. | | | |
|---|---|---|---|---|
| | Powder "A" (dried). | | Powder "B" (dried). | |
| | A.S.T.M. | B.S.S. | A.S.T.M. | B.S.S. |
| (days) | | | | |
| 1 | 97·3 | 97·4 | 122·2 | 151·1 |
| 4 | 228 | 211 | 275 | 303 |
| 6 | 299 | 270 | 347 | 373 |
| 8 | 365 | 322 | 408 | 435 |
| 11 | 460 | 389 | 484 | 511 |

The greater absorption for the B.S.S. fabric-filled discs ("B") than for the corresponding A.S.T.M. ones, is probably due to the removal of the resin skin exposing the fibres of the filler and allowing rapid absorption. With the wood-flour filled specimens ("A"), after an initial similar value, the A.S.T.M. disc showed a more rapid absorption despite its smaller area—7·07 sq.in. as compared with the B.S.S. disc's 7·93 sq.in. This may be connected with the difference in curing time. Similar conclusions may be drawn from the constants *P* given in Table 6. Comparisons made after thus allowing for the specimen thickness, show differences which are probably due to factors just mentioned. The agreement between the values for *P* for the high shock resistant moulding, preheated for B.S.S. and not preheated for A.S.T.M., is most likely fortuitous.

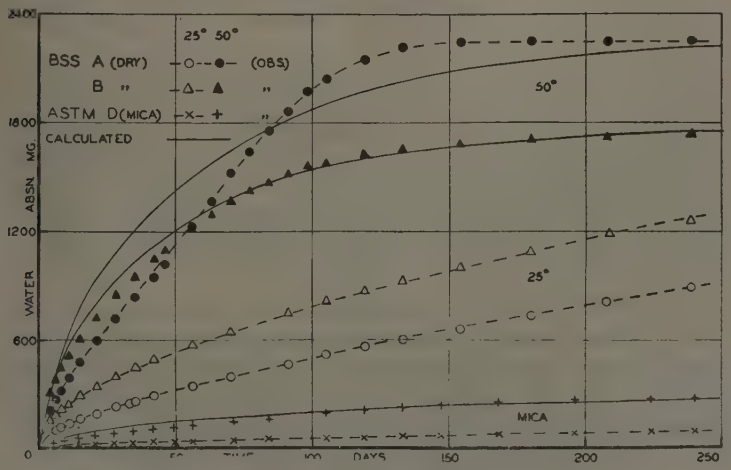


FIG. 3.—Specimens immersed at 25° and 50°C.

(vi) *Tests Using Small Specimens*

Most of our experiments have been made using the conventional mouldings, but a short test was carried out with much smaller specimens. These were prepared by grinding pieces cut from $\frac{1}{8}$ in.

thick A.S.T.M. discs in a jig similar to the one described by Shearman (16), and used for making his test pieces for mechanical tests. The size of specimen we used was 40-45 mm. by 10 mm. by 1 mm., both sides being ground.

Powders "A," wood-flour filled, and "B," fabric-filled, were used. The results are shown graphically in Fig. 4.

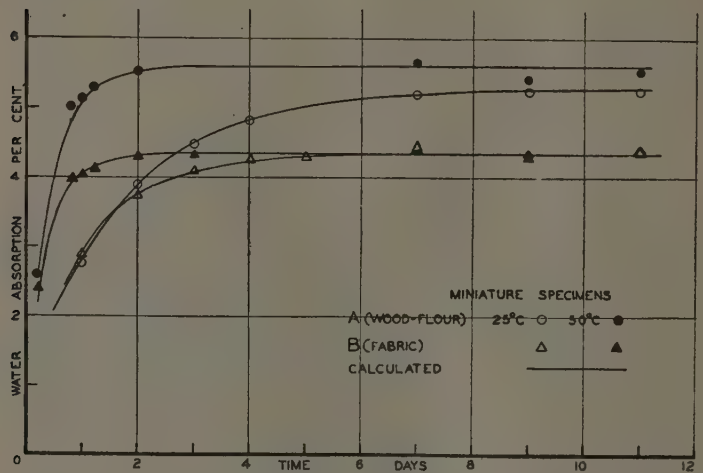


FIG. 4.—Immersion of miniature specimens at 25° and 50°C.

More extensive tests would be necessary before conclusions could be drawn with safety regarding such matters as the differences between total absorptions at different temperatures. The reversal of the relative absorptions of the wood-flour filled and the fabric filled materials between the initial determination and the later ones has been discussed more fully in Section 3 (v), where long immersion tests on full-size specimens are described. It is clear that with the miniature specimen used absorption is virtually complete in a comparatively short time, only 7 days being required at 25° and 3 days at 50°C. It is unlikely that these periods would be sufficient for water-resistant materials such as mica-filled phenolics.

It seems anomalous that these 1 mm. thick specimens should apparently reach saturation in a week at 25°C. while the pieces only 0·15 mm. thick used by Shearman were apparently not saturated in a fortnight (see Table 3 earlier). It is possible he used surface shavings while his filings were more truly representative of the whole moulding.

(vii) *Effect of Moisture Content of Powder*

As already mentioned, there is no published information on the extent to which the moisture content of a moulding powder influences the water absorption of moulded specimens. If the effect is considerable this factor will be of importance in drawing up a specification for two reasons. First, some conditioning procedure should be laid

down if results of a test are to indicate a property of the powder independent of normal variations of prior treatment. Second, the moisture content of powders may be changed not only by direct pre-heating and such commonly adopted devices as breathing during moulding, but also by chance variation in the time taken to load and close the mould.

To determine the effect of changing the moisture content of a powder, on the water absorption of the resultant moulding, the following experiment was carried out:

The two powders used, "E" and "F," contained wood-flour and canvas fillers respectively. Both powders were used with two moisture contents. Owing to the tendency of the thicker mouldings to become domed soon after pressure was released, mouldings of "E" with the higher moisture content were cooled to 120°C. before ejection, the mould being transferred rapidly to a press with cold platens at the end of the 15 minutes normal cure. With powder "F," all mouldings were ejected hot but immediately pressed between cold platens with 2,000 lb./sq.in. pressure. All A.S.T.M. discs were ejected hot.

Conditioning of specimens was according to the specification—1 hr. at 50°C. for B.S.S., 24 hrs. at 50°C. for A.S.T.M.

TABLE 8.—WATER ABSORPTION AND MOISTURE CONTENT OF POWDER

| Material. | Water Absorption (mg. per specimen) | | | |
|---|---|---|---|---|
| | "E." | | "F." | |
| Moisture Content (per cent.) .. | 5·3 | 1·95 | 5·6. | 2·4. |
| B.S.S. (7 days) .. .. | 166 | 106 | 328 | 167 |
| A.S.T.M. (7 days) .. .. | 106 | 102 | 237 | 163 |
| ,, (1 day) .. .. | 35 | 34 | 70·3 | 53·2 |

Table 8 shows that drying powders by pre-heating can cause an appreciable reduction in water absorption. Alternatively this can be regarded as indicating that a powder which initially would have passed the water absorption requirement of a specification, may fail to do so if the initial low moisture content is not maintained.

(viii) *Effect of Conditioning Specimens*

Unless a specification covers the treatment of a specimen from the time it is moulded until the test commences, the conditioning treatment given to a specimen should be sufficient to annul its normal previous history. The B.S.S. conditioning period of 1 hr. at 50°C. is apparently designed to remove surface moisture only, while 24 hrs. at 50°C., as specified by A.S.T.M., is meant to dry the specimen to a standard condition. In neither specification is there any limit to the time which may elapse between moulding and conditioning the specimen.

To find whether the conditioning specified was sufficient to cancel the effect of a severe but by no means improbable treatment of the specimens, the following test was made:

Slightly dried powders were used; "A," a wood-flour filled material, had a moisture content of 1·8 per cent.; "B," a fabric-filled powder, had 4·1 per cent.

The specimens after moulding (and machining for the B.S.S.), were divided into two sets; one was conditioned and tested according to the time schedule adopted for most of our tests, the other set was first stored for 14 days at 25°C. and 75 per cent. relative humidity and then conditioned and tested.

TABLE 9.—WATER ABSORPTION AND CONDITIONING TREATMENTS

| — | Powder "A." | | | Powder "B." | | |
|---|---|---|---|---|---|---|
| | Absorption. | | Decreased Absorption After 14 Days at 75% R.H. | Absorption. | | Decreased Absorption After 14 Days at 75% R.H. |
| | No Pre-treatment. | 14 Days' Storage at 75% R.H. | | No Pre-treatment. | 14 Days' Storage at 75% R.H. | |
| | mg. | mg. | % | mg. | mg. | % |
| B.S.S. (7 days soaking)— | | | | | | |
| 1 hr. conditioning | 96 | 71 | 26 | 197 | 139 | 29 |
| 24 hrs. conditioning | 101 | 88 | 13 | 213 | 180 | 15 |
| A.S.T.M. (24 hrs. conditioning)— | | | | | | |
| 1 day soaking .. | 32·2 | 32·0 | 0·6 | 53·2 | 51·5 | 3·2 |
| 8 days soaking .. | 108 | 94 | 12·5 | 183 | 162 | 11·5 |

The results in Table 9 indicate that even when specimens had been conditioned for 24 hours the fortnight at 25°C. and 75 per cent. relative humidity was sufficient to decrease the water absorption over a week by 11-15 per cent. With 1-hr. conditioning the storage decreased the absorption by 26-30 per cent. With the 24-hr. soaking of the A.S.T.M. the difference was only slight, confirming the results of Kline, Martin, and Crouse (8).

Two conclusions can be drawn. If the short period of soaking is accepted the A.S.T.M conditioning period may be sufficient, but even then it would be desirable to place some restriction on the treatment a specimen may receive between moulding and testing. This certainly should be done if the longer soaking period is adopted. The conditioning required by the B.S.S. test is inadequate unless treatment of the moulding is to be rigidly defined.

Choice of the best drying period should be based on a knowledge of the rate of drying of the specimens. Discs of A.S.T.M. dimensions moulded from powders "A" and "B" were dried at 50° or 100°C. and weighed periodically. The results have been graphed in Fig. 5 and show that the loss of moisture is slow and that specimens lose less moisture when made from dried powder. In contrast to water absorption, the wood-flour filled mouldings of "A" lost weight more rapidly during the conditioning period than did those of the fabric-filled "B," and though the powder of "A" contained less moisture, its mouldings lost a greater amount than did those of "B." The constants given in Table 10 were used to calculate the curves shown

as full lines in Fig. 5. These curves agree moderately well with the experimental points, the earlier values being the farthest out, and indicate that diffusion of water to the surface of the disc is the process which governs the rate of moisture loss.

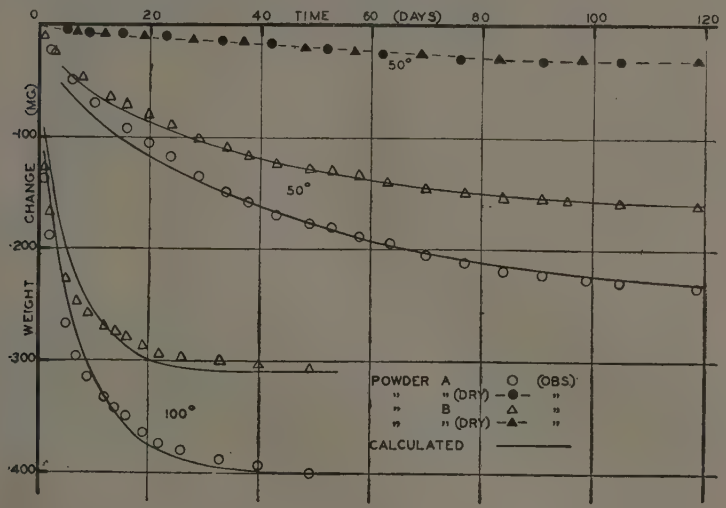


FIG. 5.—Drying A.S.T.M. specimens at 50° and 100°C.

TABLE 10.—DIFFUSION CONSTANTS (EQUATION B) FOR DRYING

| Powder. | Moisture Content. | Temp. | *S* | *K* |
|---|---|---|---|---|
| | % | °C. | mg. | 1/day. |
| "A" .. | 2·2 | 50 | 35 | (not calc.) |
| | 5·2 | 50 | 245 | 0·022 |
| | 5·6 | 100 | 400 | 0·13 |
| "B" .. | 4·5 | 50 | 35 | (not calc.) |
| | 7·0 | 50 | 165 | 0·027 |
| | 7·8 | 100 | 310 | 0·16 |

Another aspect of drying is of importance since the A.S.T.M. sets out a procedure for reconditioning specimens after they have been immersed, in order to ascertain whether there has been any loss of water-soluble material. In view of the very slow loss of moisture from specimens made from dried powders, we measured the moisture losses after discs had been immersed in water for 24 hours or for 7 days after the standard conditioning of 24 hours at 50°C. The results obtained with powder "J" have been graphed in Fig. 6, and the figures obtained with this material and powders "A" and "B" in the first few days' drying are set out in Table 11. It is apparent that the difference between the conditioned and reconditioned weights is dependent on the moisture content of the moulding powder and not on a loss of water-soluble material.

TABLE 11.—SOAKING AND DRYING SPECIMENS

| Powder. | Moisture Content. | Difference from Conditioned Weight After— | | |
|---|---|---|---|---|
| | | Soaking 24 hrs. at 25°C. | Redrying 24 hrs. at 50°C. | Redrying 72 hrs. at 50°C. |
| | % | mg. | mg. | mg. |
| "A" .. | 4·6 | 28·8 | — 2·7 | —15·6 |
| | 1·4 | 28·6 | 4·4 | 2·2 |
| "B" .. | 8·1 | 52·6 | — 5·3 | —25·7 |
| | 4·1 | 49·8 | 7·6 | 4·6 |
| "J" .. | 4·2 | 70·6 | — 3·1 | .. |
| | 2·3 | 78·8 | 8·8 | .. |

(ix) *Effect of Moulding Pressure and Use of Pressure Bar*

A test was made to find whether the limits of moulding pressure allowed by B.S.S. 771, 1-2 tons per sq. in., made any appreciable difference to the water absorption of the mouldings. At the same time the effect of a pressure bar was examined since this is sometimes used as a means for ensuring mouldings of correct thickness, and its use is not specifically excluded in the A.S.T.M. specification. With

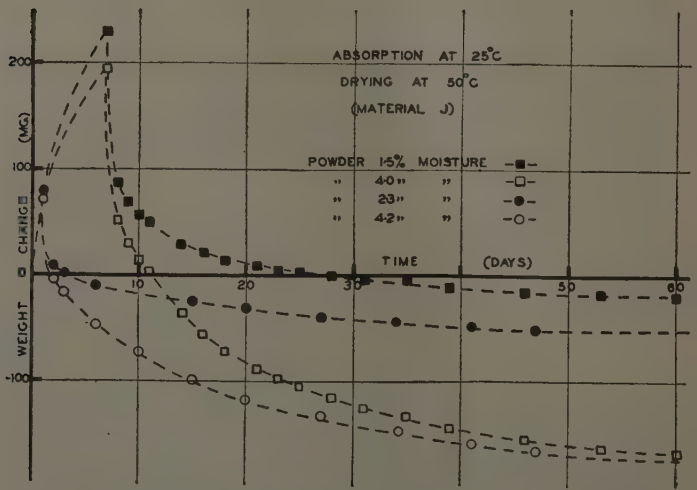


FIG. 6.—Specimens from material "J" immersed at 25° and dried at 50°C.

a pressure bar the platen rests on the bar and chase as well as on the forces when the moulding is of correct size. If the charge moulded is too small, or if material can flow away in the clearance between

forces and chase, the pressure on the moulding may differ from that apparently exerted. In extreme cases an obviously defective moulding will be produced.

In the first test the B.S.S. was followed, but specimens were conditioned 24 hours at 50°C. before immersion. Two samples of a wood-flour filled powder "G" were used, differing in flow properties, but as the mould used gave very little flash from either, the results have been averaged. Two specimens of each powder were used for each condition. Moulding was at 155°C ± 3°, at the pressure indicated, curing being 15 minutes for the hard flowing material and 20 minutes for the soft, the extra time being allowed in order to minimize doming which tended to occur though the moisture contents of the two powders were only 1·6 and 2·1 per cent. respectively, the latter being for the softer material. The charge used at first was sufficient to give a moulding of the desired thickness with no pressure bar in use. The results are given in Table 12.

TABLE 12.—EFFECT OF MOULDING PRESSURE ON WATER ABSORPTION

*B.S.S. Type Test with Powder "G"*

| Charge. | Pressure. | Relative Density. | Thickness. | Water Absorption. | |
|---|---|---|---|---|---|
| | | | | 1 Day. | 7 Days. |
| g. | lb./sq. in. | | in. | mg. | mg. |
| 31·5 | 2,000 | 1·337 | 0·449 | 50·3 | 121·6 |
| 31·5 | 4,500 | 1·338 | 0·449 | 46·4 | 116·8 |
| 29·0 | „ | 1·337 | 0·412 | 44·4 | 113·0 |
| 31·5 | „ (Bar) | 1·338 | 0·449 | 47·0 | 117·9 |
| 29·0 | „ (Bar) | 1·260 | 0·438 | 48·4 | 124·2 |

The results show a slightly greater absorption with the lower pressure though this gave no significantly lower density. The smaller charge led to increased water absorption and definitely reduced density when a bar was used: the moulding appeared perfect.

A similar test was carried out using A.S.T.M. sized specimens and moulding all for 6 minutes at 155-160° and 3,000 lb. per sq. in. Materials were powders "H" wood-flour filled, and "B" high shock resisting, with moisture contents 4·6 and 6·9 per cent. respectively. The results are shown in Table 13.

TABLE 13.—EFFECT OF WEIGHT OF CHARGE ON WATER ABSORPTION

*A.S.T.M. Type Test*

| Powder. | Charge. | Thickness. | | Relative Density. | | Water Absorption (7 Days). | |
|---|---|---|---|---|---|---|---|
| | | Bar. | Normal. | Bar. | Normal. | Bar. | Normal. |
| | g. | in. | in. | | | mg. | mg. |
| "H" .. | 9·2 | 0·129 | 0·129 | 1·373 | 1·374 | 107·6 | 107·8 |
| | 8·9 | 0·126 | 0·124 | 1·369 | 1·371 | 107·5 | 107·7 |
| | 8·6 | 0·122 | 0·121 | 1·356 | 1·369 | 114·9 | 110·4 |
| | 8·3 | 0·122 | 0·114 | 1·306 | 1·373 | 128·9 | 113·1 |
| "B" .. | 9·2 | 0·123 | 0·121 | 1·377 | 1·388 | 175·3 | 170·7 |
| | 8·9 | 0·121 | 0·116 | 1·369 | 1·386 | 175·4 | 171·4 |
| | 8·6 | 0·121 | 0·117 | 1·360 | 1·390 | 182·4 | 167·2 |
| | 8·3 | 0·123 | 0·109 | 1·284 | 1·391 | 362·3 | 175·9 |

The surface finish of the lighter weight discs moulded with the pressure bar was slightly inferior to the others, and one of each duplicate for each material at the lightest charge was incompletely filled out, being crumbly at one spot on the edge. The results show that the use of a pressure bar can lead to decreased densities and increased water absorptions if light weight charges are used, and the mouldings may not appear defective.

(x) *Effect of Temperature of Immersion.*

The temperature of the water in which discs are immersed will obviously have a great influence on the rate at which it is absorbed, though it may not greatly influence the total uptake. Since the standard tests are essentially a measure of the rate so far as moulded phenolics are concerned, temperature control will be of great importance. In the A.S.T.M test the temperature and limits are set out as 25°C. ± 2° whereas 20°C. ± 5° is allowed by the B.S.S.

A simple test was made using powders "G" (wood-flour filled) and "F" (canvas filled) moulded into discs of the A.S.T.M. size. After 24 hours drying at 50°C. these were immersed in water baths at different temperatures, five specimens of each powder being tested at each temperature.

The results set out in Table 14 show that the 10° range permitted by B.S.S. is too liberal and a range of ± 2° is the most that should be allowed for the results to be reasonably accurate, though even this will permit a variation greater than 5 per cent.

The choice of testing temperature must be based on other considerations and in Australia the ambient summer temperatures make 25°C. more simply attained than a lower figure.

TABLE 14.—EFFECT OF TEMPERATURE ON IMMERSION

| Powder. | Time of Immersion. | Water Absorption After Immersion at— | | | | |
|---|---|---|---|---|---|---|
| | | 10°C. ± 1°. | 14°C. ± 2°.* | 20°C. ± 1°. | 25°C. ± 1°. | 30°C. ± 1°. |
| | days. | mg. | mg. | mg. | mg. | mg. |
| "G" | 1 | 18·1 | 18·5 | 24·9 | 30·0 | 37·3 |
| | 2 | 25·8 | 26·8 | 36·3 | 43·4 | 54·4 |
| | 3 | 31·3 | 33·1 | 45·2 | 54·5 | 69·3 |
| | 7 | 48·3 | 52·2 | 72·6 | 88·8 | 116·2 |
| "F" | 1 | 31·2 | 34·7 | 46·8 | 57·8 | 66·3 |
| | 2 | 50·5 | 54·1 | 73·6 | 88·5 | 103·4 |
| | 3 | 63·5 | 70·3 | 95·7 | 116·0 | 135·3 |
| | 7 | 102·8 | 121·6 | 168·4 | 204·5 | 241·3 |

* Controls on the thermostat were inadequate and average temperature was probably lower than shown.

## 4. Conclusions

The work at present reported and the papers reviewed lead to conclusions which should assist in the choice of a suitable method for testing the water absorption of phenolic mouldings.

Before setting up a specification test, it is essential that the testing authorities should recognize the two independent factors involved, rate of penetration and saturation level, and decide which is to be measured, particularly if different plastics are to be compared. The present type of test as set out by both A.S.T.M. and B.S.S., indicates only the initial rate of absorption, and results are not comparable over a wide range of plastics. Thin specimens or filings may be suitable for finding saturation values in reasonably short periods, but insufficient work has been carried out to indicate the scope or limitations of such tests. Absorption from a saturated atmosphere is slower than from water, but by either method almost the same saturation level is ultimately reached.

With regard to the conventional method of test, both A.S.T.M. and B.S.S. procedures are sensitive to the history of the moulding powder and moulding prior to conditioning, though the A.S.T.M conditioning does more to eliminate variations than does the short period required by B.S.S. Limits should be set to the time allowable between moulding the specimen and conditioning it for test, and to the humidity to which specimens may be exposed in that period. Moulding pressure should be limited to a narrower range than that allowed by B.S.S. A fully positive mould should be specified.

A disc of the dimensions required by A.S.T.M. is preferable to the thicker, machined disc, for the latter is more difficult to mould with some powders, and the machining achieves no real advantage.

Since an arbitrary time must be chosen for a standard test, 24 hours should be adopted when different types of plastics are to be compared. A longer period, 7 days, is preferable when comparing similar plastics with slow rates of penetration.

Phenolic plastic discs after soaking are not subject to large evaporation losses within the specified period of up to 15 minutes after removing superficial water, though several minutes must be allowed initially for air drying of machined specimens.

For Australian conditions a higher immersion temperature than 20°C. is advisable. The 10° range permitted by B.S.S. is too wide. The A.S.T.M. conditions 25°C. $\pm$ 2° for immersion would be satisfactory.

Results should be expressed as weight absorbed per specimen provided no significant variation of area is allowed. Expressing initial water absorption as a percentage of the weight of the specimen has nothing to recommend it.

An extension of the specification tests to cover a method for determining the moisture content of moulding powders, could well be considered. It should be related to a procedure for conditioning powders to equilibrium with a standard low relative humidity before moulding.

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# A Simple Method of Testing Glue Lines in Tension

*By A. W. Rudkin, B.Sc.**

*Summary*

A method is described for testing glue lines in tension, using, with only slight modifications, the same apparatus as is used for testing glue lines in shear, which is standard equipment in all laboratories concerned with the testing of glued joints.

The test specimens are made up in the form of right-angled crosses in a press-box slightly modified from that normally used for making standard lap joints for shear tests. The modified press-box can still be used for making standard shear strength test specimens.

After reconditioning, the specimens are fitted into a specially designed shackle, which can be fitted into a standard testing machine of the type normally used for shear strength tests. When load is applied to the shackle in the usual manner, it is transmitted to the specimen in a direction normal to the plane of the glue line, so that the tensile failing load can be read off in the same way as shear failing loads are ordinarily read.

Results of tests by this method on a number of types of joints were statistically compared with results of standard shear strength tests on joints made with the same materials, and it was found that the results of the tests in tension were reproducible with at least as high a degree of accuracy as those of standard tests in shear.

## 1. Introduction

It is well known that practically all types of glued joints are very much stronger in shear than in tension, and for this reason engineers, when designing structures embodying glued joints or laminated members, try to ensure that the glue line is not subjected to severe tensile stresses. Hence most adhesive specifications do not call for tests on the tensile strength of joints, and equipment for this purpose is only available in a few large laboratories.

In the course of a project undertaken by the Council's Division of Aeronautics (Dale, 1945), however, it was found desirable to use laminated members in situations where considerable tensile stresses perpendicular to the plane of the glue line could not be avoided, and hence, when the Division of Forests Products was asked to carry out tests to determine the most suitable adhesives for use in this project, it was necessary to devise means for comparing the tensile strength of joints made with the various adhesives proposed. No apparatus for this purpose was readily available, and some of the materials used in the experiment (Rudkin, 1946), viz. asbestos cement sheet and "Masonite", were not suitable for making the type of joints used for tensile strength tests at, for instance, the Canadian Forests Products Laboratory (Wakefield, 1943).

## 2. Method

The materials to be glued (mountain ash, asbestos cement sheet, and "Masonite") were cut into slips 6½ in. by 1 in., the length being parallel to the grain in the case of the wood. In one series of tests the slips were 3/16 inch thick; in another series, the mountain ash

* An officer of the Division of Forests Products.

slips were $\frac{3}{8}$ inch thick, and the other materials, which were supplied in sheets 3/16 inch thick, were glued on to sawn sheets of mountain ash 3/16 in. thick, making up a total thickness of $\frac{3}{8}$ inch, before cutting to the requisite size.

The adhesive was applied to the gluing surfaces in the usual way and the slips were placed in the press-box as shown in Fig. 1A, and pressed in the usual manner. This produced a cross-shaped specimen as shown in Fig. 1B, with the glue-line area exactly 1 inch square. A press-box of the type normally used for making standard shear strength test specimens (Standards Association of Australia, 1941) is shown in Fig. 2 for comparison. Fig. 3 is another view of the press-box shown in Fig 1A, containing standard lap-joints for shear tests, demonstrating that the box can still be used in the normal way after being modified to take glue-line tensile strength test specimens.

FIG. 1A.—Tensile strength test specimens undergoing pressure in adapted press-box.

After reconditioning, the specimens were fitted into the shackle as shown in Fig. 4, and packed tightly with metal shims to minimize bending stress. The shackle was then fitted into the grips of the testing machine as shown in the figure, and the load was applied in the usual manner until the joint failed. Fig. 5 shows a standard lap

joint fitted into the same machine in readiness for testing in shear, demonstrating that the method of applying the load is essentially the same whether the joint is tested in shear or in tension.

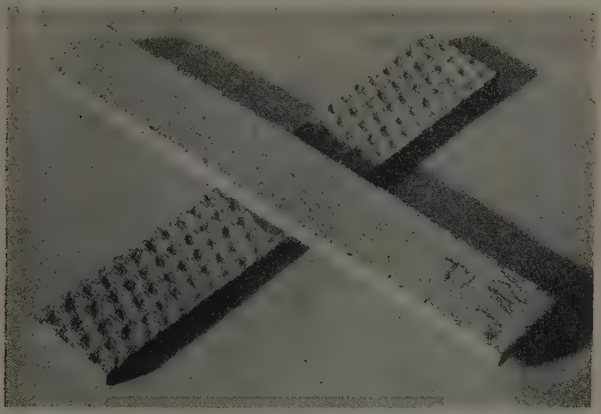

FIG. 1B.—Specimen for tensile strength test.

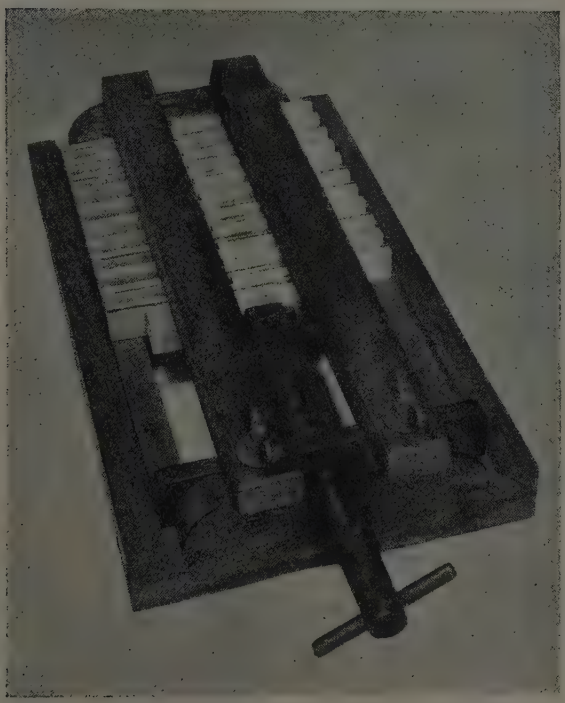

FIG. 2.—Shear strength test specimens in standard press-box.

### 3. Discussion of Results

An estimate of how accurately results obtained by the method described above correspond to the true tensile strength of the joint could only be made by comparing them with the results obtained with similar materials by methods of proven reliability. This has unfortunately not been possible.

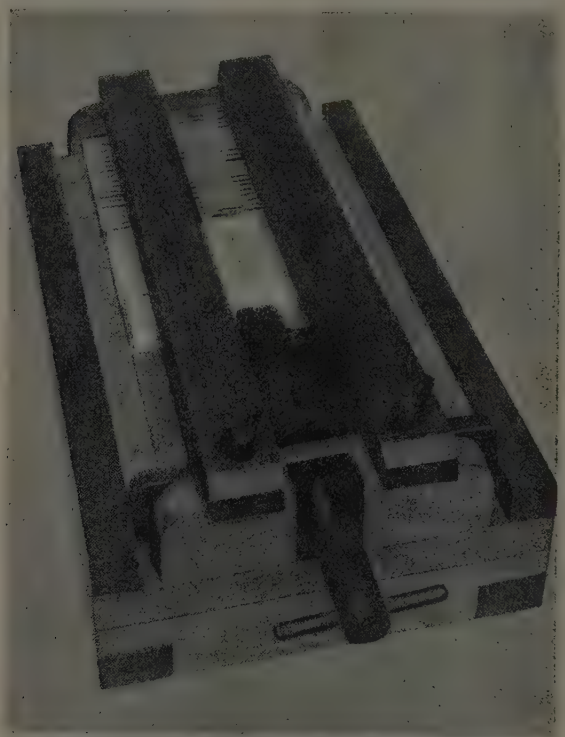

FIG. 3.—Shear strength test specimens undergoing pressure in press-box adapted for making tensile strength test specimens.

Tension tests on the glue lines of phenol-formaldehyde bonded plywood carried out at the Canadian Forest Products Laboratories (Wakefield, 1943) usually gave results of the order of 500-800 lb. per sq. in. on yellow birch, 150-300 lb. per sq. in. on sitka spruce and 300-750 lb. per sq. in. on western white pine; strengths of over 1,200 lb. per sq. in. were recorded on individual specimens. In the tests by the method described in this paper, results on mountain ash (*Eucalyptus regnans*) bonded to mountain ash with good quality wood-working adhesives ranged from 138 to 265 lb. per sq. in., and in preliminary tests on coachwood (*Ceratopetalum apetalum*), radiata pine (*Pinus radiata*), rimu (*Dacrydium cupressinum*), and myrtle beech (*Nothofagus cunninghamii*), to check the practicability of the

method, results were usually of the order of 100 lb. per sq. in. Percentage adhering wood fibre was usually slightly higher than in the Canadian tests. These figures indicate that results by the new method may be lower than the true tensile strength of the joints. This may be due to failure to eliminate bending stress to the same extent as in the Canadian tests.

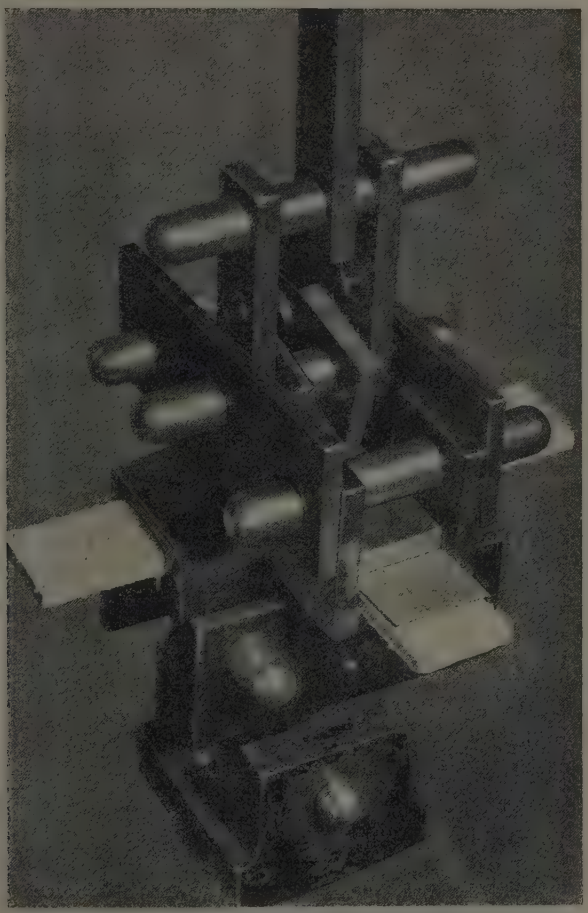

FIG. 4.—Tensile strength test specimen fitted into shackle in testing machine.

Fortunately it is rarely necessary, either in specification testing of adhesives or in more fundamental work on adhesion, to determine the absolute shear or tensile strength of a joint. In specification testing, it is usually sufficient to determine whether a given adhesive gives joints equal or superior to those given by adhesives found suitable

in service tests, and, in more fundamental studies, whether a given change in adhesive formulation or gluing conditions produces a reduction or an increase in joint strength. For these purposes the main desiderata are:—

(i) The results should be sufficiently accurately reproducible to enable the mean of a small number of tests (usually five in specification testing) to be accepted as a reasonably accurate estimate of the mean value that would be obtained in an indefinitely large number of tests.

(ii) The results of the test should be positively correlated to a high degree with the true shear or tensile strength as the case may be.

In making standard shear strength tests on plywood or on glued joints, for instance, it has to be remembered that there is no constant value $S$ that can be defined as the shear strength of the glue line in terms of breaking stress per unit area. The failing load, $F$, of the specimen depends not only on the adhesive, the adherends, the gluing conditions, and the area $A$, but also on the shape of $A$ and the thickness, $T$, of the specimen (De Bruyne, 1944). Thus for a rectangular specimen, the value of $F$ is a linear function of the width, $W$, of the specimen, but not of the length of overlap, $L$ (length being defined as the dimension parallel to the direction of loading), $dF/dL$ tending to very low positive values or to zero as $L$ increases. For fairly thin specimens at least, $F$ also increases with $T$; again $dF/dT$ tends to very low positive values or to zero as $T$ increases. For these reasons the "shear strengths" of different adhesives, &c., are arbitrarily compared by determining the failing loads of lap joints with a specified overlap (usually one inch square) and made from rectangular slips of a specified length and thickness. The dependence on length of overlap is due to stress concentrations at the ends of the joint owing to differences in *ductility* between the adhesive and the adherends (De Bruyne, 1944); the dependence on thickness of the specimen is due mainly to the fact that bending stresses are not completely eliminated in standard methods of testing.

Hence a proposed method of determining tensile strength can be considered sufficiently accurate for most practical purposes if it can be shown that:—

(i) Variation among specimens made with the same materials under the same conditions is no greater than that of standard shear strength test results on the same type of joint, thus meeting the criterion of reproducibility.

(ii) Variation between groups of specimens made with different materials or under different conditions is large compared with variation within the groups, indicating that between-group variation is not random and is therefore correlated with differences between the strength characteristics of the various types of joints.

Results of a series of tensile strength tests are set out in Table 1, and results of a series of shear strength tests on joints made with similar materials are set out for comparison in Table 2. A statistical analysis was made of these to determine whether the method met the above criteria.

The statistical analysis showed that, with specimens $\frac{3}{8}$ inch thick, the coefficients of variation of shear and tensile strength test results were approximately equal. The standard deviation was actually smaller in the case of the tensile than of the shear strength test results, i.e. the absolute variability of the former was less than that of the latter (slightly less than one half), even though the percentage variation was slightly greater owing to the much smaller mean values obtained in the tensile tests. The difference in absolute variability was highly significant.

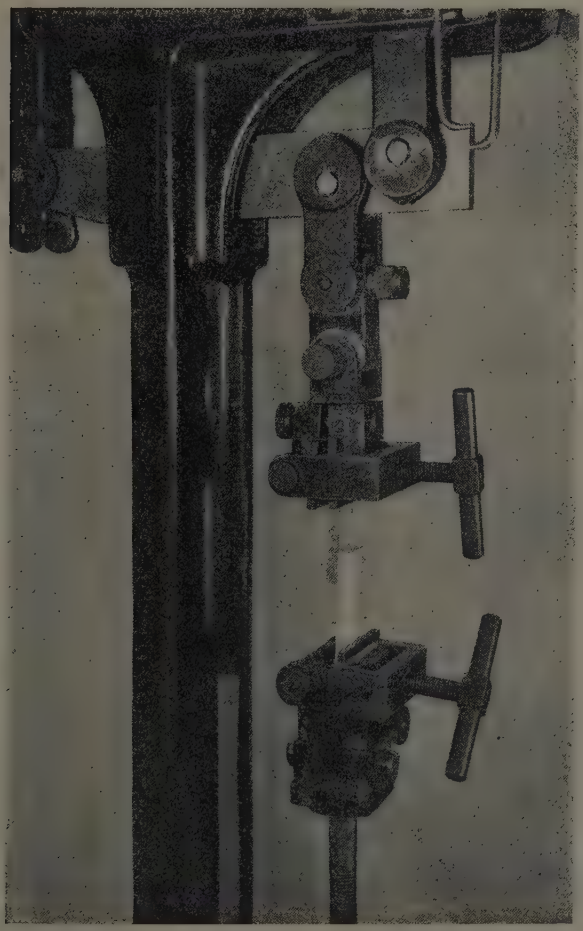

FIG. 5.—Shear strength test specimen fitted into testing machine.

With the specimens 3/16 inch thick, the coefficient of variability of the tensile strength test results was appreciably greater than that of the shear strength test results, the difference being significant at the 5 per cent. level, but even in this case the absolute variability of the tensile test results was rather less than $\frac{2}{3}$ of that of the shear test.

### *Key to Tables*

The following abbreviations are used to describe gluing surfaces:—

W = kiln-dried and reconditioned mountain ash.
S = smooth face of asbestos cement sheet.
R = screen (rough) face of asbestos cement sheet.
M = screen face of "Masonite".

TABLE 1.—TENSILE FAILING LOADS OF GLUED JOINTS

| Adhesive | Gluing Surfaces | Thickness of Slips | Number of Specimens | Tensile Failing Loads | | |
|---|---|---|---|---|---|---|
| | | | | Min. | Max. | Mean |
| | | in. | | lb. | lb. | lb. |
| Casein cement .. | W–W .. | $\frac{5}{16}$ | 6 | 138 | 265 | 188·7 |
| ,, ,, .. | ,, .. | $\frac{3}{8}$ | 5 | 135 | 254 | 227·0 |
| ,, ,, .. | R–W .. | $\frac{5}{16}$ | 3 | 98 | 110 | 103·3 |
| ,, ,, .. | ,, .. | $\frac{3}{8}$ | 4 | 29 | 103 | 82·5 |
| ,, ,, .. | R–R .. | $\frac{5}{16}$ | 3 | 40 | 56 | 46·0 |
| ,, ,, .. | ,, .. | $\frac{3}{8}$ | 5 | 124 | 167 | 141·8 |
| ,, ,, .. | R–S .. | $\frac{5}{16}$ | 3 | 18 | 33 | 27·3 |
| ,, ,, .. | ,, .. | $\frac{3}{8}$ | 5 | 72 | 106 | 96·2 |
| ,, ,, .. | S–M .. | $\frac{5}{16}$ | 5 | 43 | 61 | 52·6 |
| ,, ,, .. | ,, .. | $\frac{3}{8}$ | 5 | 65 | 118 | 97·4 |
| ,, ,, .. | Coachwood .. | $\frac{5}{16}$ | 5 | 113 | 162 | 134·6 |
| ,, ,, .. | Radiata pine— | | | | | |
| | Sample A. .. | ,, | 3 | 94 | 174 | 145·0 |
| ,, ,, .. | Sample B. .. | ,, | 6 | 61 | 69 | 63·0 |
| ,, ,, .. | Rimu .. | ,, | 6 | 107 | 123 | 115·2 |
| ,, ,, .. | Myrtle beech | ,, | 6 | 80 | 106 | 97·8 |
| Rubber cement A. | W–W .. | $\frac{3}{8}$ | 5 | 48 | 88 | 72·2 |
| ,, ,, | R–W .. | ,, | 5 | 115 | 144 | 122·2 |
| ,, ,, | R–R .. | ,, | 5 | 78 | 150 | 113·2 |
| ,, ,, | R–S .. | ,, | 5 | 105 | 160 | 122·6 |
| ,, ,, | S–M .. | ,, | 5 | 58 | 126 | 93·0 |
| ,, ,, | W–W* .. | ,, | 5 | 54 | 132 | 99·2 |
| ,, ,, | R–W* .. | ,, | 5 | 115 | 159 | 135·6 |
| ,, ,, | R–R* .. | ,, | 5 | 109 | 150 | 124·2 |
| ,, ,, | R–S* .. | ,, | 5 | 90 | 137 | 109·6 |
| ,, ,, | S–M* .. | ,, | 5 | 38 | 131 | 91·0 |
| Rubber cement B. | W–W .. | $\frac{5}{16}$ | 7 | 49 | 83 | 63·2 |
| ,, ,, | ,, .. | $\frac{3}{8}$ | 5 | 55 | 122 | 81·4 |
| ,, ,, | R–W .. | $\frac{5}{16}$ | 6 | 57 | 78 | 68·3 |
| ,, ,, | ,, .. | $\frac{3}{8}$ | 5 | 92 | 151 | 126·8 |
| ,, ,, | R–R .. | $\frac{5}{16}$ | 5 | 47 | 68 | 53·8 |
| ,, ,, | ,, .. | $\frac{3}{8}$ | 5 | 53 | 135 | 101·2 |
| ,, ,, | R–S .. | $\frac{5}{16}$ | 4 | 96 | 131 | 118·5 |
| ,, ,, | ,, .. | $\frac{3}{8}$ | 5 | 97 | 125 | 107·6 |
| ,, ,, | S–M .. | $\frac{5}{16}$ | 5 | 67 | 90 | 81·8 |
| ,, ,, | ,, .. | $\frac{3}{8}$ | 5 | 62 | 96 | 79·6 |
| Liq. phenolic resin | W–W .. | $\frac{5}{16}$ | 5 | 52 | 101 | 77·8 |
| ,, ,, | R–W .. | ,, | 5 | 54 | 90 | 67·8 |
| ,, ,, | R–R .. | ,, | 5 | 45 | 67 | 51·2 |
| ,, ,, | R–S .. | ,, | 4 | 18 | 42 | 28·3 |
| ,, ,, | S–M .. | ,, | 5 | 47 | 83 | 65·4 |

* An extended sample of rubber cement A was used.

results, the high percentage variability of the former being due to their low mean. The difference in absolute variability was again highly significant.

TABLE 2.—SHEAR FAILING LOADS OF GLUED JOINTS

| Panel Number* | Adhesive | Gluing Surfaces | Thickness of Slips | Number of Specimens | Shear Failing Loads | | |
|---|---|---|---|---|---|---|---|
| | | | | | Min. | Max. | Mean |
| | | | in. | | lb. | lb. | lb. |
| | Casein cement .. | W–W | 3/16 | 5 | 660 | 932 | 832·2 |
| | ,, ,, .. | ,, | 3/8 | 4 | 880 | 1,176 | 1,074·75 |
| | ,, ,, .. | R–W | 3/16 | 6 | 180 | 230 | 210·0 |
| C1FW .. | ,, ,, .. | ,, | 3/8 | 5 | 128 | 225 | 179·8 |
| C2FW .. | ,, ,, .. | ,, | ,, | 5 | 61 | 204 | 151·0 |
| | ,, ,, .. | ,, | ,, | 5 | 301 | 460 | 389·6 |
| | ,, ,, .. | R–R | 3/16 | 5 | 120 | 143 | 132·2 |
| C1RR .. | ,, ,, .. | ,, | ,, | 3 | 73 | 111 | 93·3 |
| C2RR .. | ,, ,, .. | ,, | ,, | 4 | 85 | 133 | 100·25 |
| | ,, ,, .. | ,, | 3/8 | 5 | 233 | 306 | 272·1 |
| | ,, ,, .. | R–S | 3/16 | 7 | 105 | 215 | 168·9 |
| C1RS .. | ,, ,, .. | ,, | ,, | 5 | 45 | 90 | 69·0 |
| C3RS .. | ,, ,, .. | ,, | ,, | 5 | 104 | 145 | 130·8 |
| | ,, ,, .. | ,, | 3/8 | 5 | 206 | 302 | 258·6 |
| | ,, ,, .. | S–M | 3/16 | 7 | 90 | 228 | 166·0 |
| C1FM .. | ,, ,, .. | ,, | ,, | 5 | 103 | 130 | 115·0 |
| C2FM .. | ,, ,, .. | ,, | ,, | 5 | 104 | 140 | 126·8 |
| | Rubber cement A. | W–W | 3/8 | 5 | 116 | 174 | 136·8 |
| | ,, ,, | R–W | ,, | 5 | 142 | 198 | 180·2 |
| | ,, ,, | R–R | ,, | 5 | 165 | 186 | 175·4 |
| | ,, ,, | R–S | ,, | 5 | 193 | 228 | 204·0 |
| | ,, ,, | S–M | ,, | 5 | 166 | 205 | 188·2 |
| | ,, ,, | W–W† | ,, | 5 | 102 | 120 | 112·0 |
| | ,, ,, | R–W† | ,, | 5 | 130 | 200 | 167·0 |
| | ,, ,, | R–R† | ,, | 5 | 172 | 225 | 200·4 |
| | ,, ,, | R–S† | ,, | 5 | 207 | 284 | 239·6 |
| | ,, ,, | S–M† | ,, | 5 | 207 | 320 | 279·8 |
| | Rubber cement B. | W–W | ,, | 4 | 124 | 260 | 192·75 |
| R1FW .. | ,, ,, | R–W | 3/16 | 5 | 62 | 92 | 77·8 |
| R2FW .. | ,, ,, | ,, | ,, | 5 | 64 | 72 | 68·2 |
| | ,, ,, | ,, | 3/8 | 5 | 82 | 210 | 134·4 |
| R1RR .. | ,, ,, | R–R | 3/16 | 5 | 117 | 138 | 131·6 |
| R2RR .. | ,, ,, | ,, | ,, | 2 | 84 | 89 | 86·5 |
| | ,, ,, | ,, | 3/8 | 4 | 136 | 172 | 149·75 |
| R1RS .. | ,, ,, | R–S | 3/16 | 4 | 25 | 76 | 40·0 |
| R2RS .. | ,, ,, | ,, | ,, | 2 | 53 | 125 | 89·0 |
| R3RS .. | ,, ,, | ,, | ,, | 5 | 120 | 133 | 125·8 |
| | ,, ,, | ,, | 3/8 | 5 | 137 | 198 | 173·0 |
| R1FM .. | ,, ,, | S–M | 3/16 | 5 | 82 | 120 | 101·8 |
| R2FM .. | ,, ,, | ,, | ,, | 5 | 122 | 152 | 134·0 |
| | ,, ,, | ,, | 3/8 | 5 | 137 | 352 | 219·0 |
| | Liq. phenolic resin | W–W | 3/16 | 5 | 640 | 838 | 755·8 |
| PB1FW | ,, ,, | R–W | ,, | 4 | 97 | 170 | 142·25 |
| PB2FW | ,, ,, | ,, | ,, | 3 | 163 | 168 | 165·3 |
| | ,, ,, | R–R | ,, | 3 | 10 | 100 | 61·7 |
| PA1RR | ,, ,, | ,, | ,, | 5 | 77 | 128 | 101·4 |
| PA2RR | ,, ,, | ,, | ,, | 5 | 90 | 123 | 102·0 |
| | ,, ,, | R–S | ,, | 3 | 85 | 105 | 93·3 |
| PA1RS | ,, ,, | ,, | ,, | 5 | 138 | 197 | 161·2 |
| PA2RS | ,, ,, | ,, | ,, | 5 | 152 | 172 | 162·8 |
| | ,, ,, | S–M | ,, | 6 | 100 | 150 | 126·7 |
| PA1FM | ,, ,, | ,, | ,, | 3 | 124 | 193 | 147·7 |
| PA2FM | ,, ,, | ,, | ,, | 3 | 104 | 160 | 139·0 |

* Where no panel number is given, the specimens were made up singly and not cut from panels.

† An extended sample of rubber cement A was used.

The analysis further showed that the results on the two thicknesses were consistent with each other, and, on analysing the combined results of the tests on both thicknesses, it was found (*a*) that there was no significant difference between the coefficients of variation, and (*b*) that the absolute variability of the tensile strength test results was lower than that of the shear strength test results, the difference being highly significant. The relevant statistical data are summarized in Tables 3 and 4.

TABLE 3.—VARIANCES OF TENSILE AND SHEAR TEST RESULTS

| Type of Test | Thickness of Slips | | |
|---|---|---|---|
| | 3/16 in. | 1/8 in. | Combined |
| Tensile (lb.) .. .. | 579 (79) | 443 (34) | 538 (113) |
| Shear (lb.) .. .. .. | 2328 (78) | 2917 (37) | 2518 (115) |
| $t$ (Pitman's test) .. .. | 6·67** | 6·48** | 9·08** |

Figures in brackets denote number of degrees of freedom.
** Significant at the 1 per cent. level.

TABLE 4.—COEFFICIENTS OF VARIATION AND STANDARD ERRORS OF TENSILE AND SHEAR TEST RESULTS

| Type of Test | Thickness of Slips | | |
|---|---|---|---|
| | 3/16 in. | 1/8 in. | Combined |
| Tensile (lb.) .. .. | 21·63 ± 1·60 | 27·67 ± 3·17 | 22·86 ± 1·43 |
| Shear (lb.) .. .. | 19·45 ± 1·43 | 19·13 ± 2·04 | 19·34 ± 1·17 |
| Difference .. .. | 2·18 ± 2·15 | 8·54 ± 3·77* | 3·74 ± 1·86 |

Weighted mean of coefficients of variation = 20·76 ± 0·91.
* Significant at the 5 per cent. level.

The over-all conclusion was that the coefficients of variation of the two types of test (shear and tensile) are approximately equal, the higher apparent coefficient of the tensile strength tests on specimens 3/16 inch thick being a chance result; whilst the absolute variability of the tensile strength test is considerably less than that of the shear strength test. For most practical purposes the absolute variability is more important than the coefficient of variation, most tests of significance being based on absolute and not on percentage deviations from the mean. Hence the proposed test meets the criterion of reproducibility.

The analysis showed also that with the thicker specimens the effects of adhesives and of gluing surfaces, and the interaction between these variables, were highly significant for both tensile and shear tests, and there was a highly significant variation of both tensile and shear strength with differences in treatment. (No attempt was made

to separate the effect of gluing surfaces and of adhesives with the 3/16 inch specimens.) This means it is highly improbable that variations among the results of tests on the different types of joint were due to chance factors, and it is therefore reasonable to assume that they were correlated with the factors being tested, i.e. with the shear strength of the joints in Table 1 and with the tensile strength in Table 2.

## 4. Conclusion

It may therefore be concluded that the method of testing the tensile strength of glued joints described herein is sufficiently accurate and reproducible for most purposes, i.e., it is probably at least as accurate and reproducible as accepted standard tests on the shear strength of glued joints.

## 5. Acknowledgments

I am indebted to Mr. J. J. Mack of the Division of Forest Products for his helpful suggestions on the design of the shackle used in the above tests, and for making the working drawing of the design finally agreed upon and supervising the manufacture of the shackle; and to Mr. R. T. Leslie of the staff of the Section of Mathematical Statistics for performing much of the mathematical work involved in interpreting the results.

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# The Variation of Maximum Crushing Strength, Maximum Tensile Strength, and Modulus of Elasticity of Hoop Pine (*Araucaria cunninghamii* Ait.) Plywood with Moisture Content

*By R. S. T. Kingston, B.Sc., B.E.**

*Summary*

Hoop pine plywood in 1/8, 3/16, and 1/4 inch thicknesses, bonded with phenol-formaldehyde, urea-formaldehyde, and casein glues, in each case has been tested in compression and tension parallel, perpendicular, and at 45° to the grain of the outer veneers. The elastic modulus has also been determined from the tensile tests.

The tests were carried out at nominal moisture contents of 8, 12, 16, and 20 per cent. and regression factors determined so that moisture corrections could be made to the corresponding strength figures for this species where necessary.

On account of the inconvenience of application of such factors, and since an additive correction would not be satisfactory in all cases, tables are included giving the strengths at each integral percentage of moisture content over the range of the observations. These are expressed as a percentage of the corresponding value at 12 per cent. moisture content.

## 1. Introduction

The mechanical properties of wood are influenced by its moisture content, and the law of variation for some static properties at normal temperatures is known to be well represented, for moisture contents below the intersection point, (2, 14) by an exponential relationship (7). For impact properties, the relationship is of a rather different nature and appears generally to follow a somewhat U-shaped curve, often having a pronounced minimum somewhere about 12 to 16 per cent. moisture content (4) although occasionally the curve rises or falls monotonically with increasing moisture content. In the case of tests on solid timber, a considerable variation of moisture content is found to occur from specimen to specimen, even after conditioning at constant temperature and the appropriate relative humidity. It is therefore considered necessary to determine suitable moisture correction figures for species under test and to correct the results of individual tests to a standard moisture content.

Hitherto, no correction for moisture content has been made to plywood test results, since it was generally understood from results of tests overseas that the correction was negligible. This belief is reflected in the Australian standard specifications for aircraft plywood (8, 9), which specify strength values without reference to moisture content except in the " moisture content " paragraph which states that it shall be between 7 and 14 per cent. It has been felt necessary, however, to check this assumption and, should the variation be of such a magnitude as to render correction necessary, to provide correction figures for plywood.

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It was decided that the species to be tested initially for this purpose should be hoop pine. If the corrections should prove of considerable magnitude it might then be necessary to test other species. On the other hand, it is possible that the corrections for solid timber could be applied directly. In this case it is desirable that this conclusion should be checked for one or two additional species.

## 2. Selection of Material

Twenty logs of hoop pine (*Araucaria cunninghamii* Ait.) were selected from ten trees cut in a number of localities in the Brisbane, Mary, and Gladstone River valleys, the Wide Bay district south of Maryborough, and the Port Clinton district north of Rockhampton. Veneer was peeled from each log in three thicknesses namely 1/24-in., 1/16-in., 1/12-in. The 1/24-in. veneer was peeled at 4–5 in. from the centre of the log, the 1/16-in. at 5–6 in. from the centre, and the 1/12-in. veneer at 6–7 in. from the centre. In this way the effect of distance from pith on the strength properties was minimized, because pith eccentricity was small in all cases. This was considered satisfactory since, in tests on solid hoop pine as an aircraft timber, no significant regression on distance from pith had been found for compressive strength parallel to the grain or for modulus of elasticity, although a regression, significant at the 5 per cent. level of probability, had been found to be present for maximum tensile strength (3). It is unlikely that small differences in distance from pith would have much effect in a softwood and it was impossible to cut the various thicknesses at random distances from the pith in various logs because these were being used for other investigations as well as the one described here. In the selection of this material, any veneer containing compression wood, compression failures, knots, or other defects likely to affect the strength, was rejected.

The veneer, when dried, was glued into three-ply sheets 19½ in. square made with each of the following glues: (*a*) a casein glue, (*b*) a urea-formaldehyde glue, and (*c*) a phenol-formaldehyde film glue. In each sheet of plywood, the three veneers were closely matched. A total of 360 sheets was prepared: that is, 18 sheets from each log comprising two for each glue in each thickness.

Two sets of specimens were cut from each sheet, specimens parallel, at 45°, and perpendicular to the grain of the face veneer, being included. It was decided to test at four nominal moisture contents, namely 8, 12, 16, and 20 per cent. These values are based on the equilibrium moisture content of spruce (*Picea sitchensis* (Bon.) Carr.) slivers placed in the room whilst at a moisture content lower than that in equilibrium with the room, so that they would adsorb moisture. The four specimens available for each glue thickness and direction of grain in each log were allotted to the four moisture contents on the assumption that the two sheets made with the same glue and thickness of veneer from material from the same log were identical. The veneer in these had been carefully matched and the reason that they were not glued into one instead of two sheets was limitation of press capacity. However, the allocation of moisture contents between sheets was continually changed, in order to obviate any possibility of a systematic difference arising.

### 3. Moisture Conditioning Treatment

The test material was conditioned in humidity controlled rooms having a temperature in all cases of between 20° and 40°C. in order to avoid damage to the plywood. With the material for test at 8 per cent. moisture content, it was found necessary to use a temperature of 37°C. in order to reduce the relative humidity sufficiently, with the equipment available. For the remaining material the conditioning temperature was in the vicinity of 30°C. The conditions in these rooms were adjusted with the aid of thin slips of sitka spruce which were placed in the room at moisture contents of about 3 per cent. below the desired value. The humidity of the room was then gradually increased until the spruce slips reached the desired moisture content. These were then weighed every day to check the conditions and new ones, also reduced to about 3 per cent. below the desired moisture content, were occasionally introduced for check purposes. The slips varied by about $\pm 0{\cdot}25$ per cent. moisture content. The value was often constant to less than $\pm 0{\cdot}1$ per cent. for some days and then a fluctuation of $\pm 0{\cdot}1$ or $\pm 0{\cdot}2$ per cent. would occur. The variation between the values for two successive days was rarely more than this although occasional larger changes occurred, necessitating an adjustment of the room setting. When sudden fluctuations in moisture content occurred, new spruce slips were introduced as a check, in case those already there were in error due to hysteresis in the relative humidity-moisture content relationship. The apparent moisture content of the specimens when equilibrium had been reached was not, of course, the same as that of the spruce. This was particularly noticeable in the case of plywood glued with synthetic resin glues where the moisture content determined by oven-drying was some 2 to 3 per cent. below that of the spruce, the reason for which was probably loss in hygroscopicity due to the exposure of the plywood to elevated temperature during pressing.

### 4. Method of Test

All tests were carried out in a temperature range of 21°C. $\pm 1°$, the specimens being given time to reach this temperature before testing, since Kollman (5) and Sulzberger (10) have shown that considerable changes occur in the strength properties of wood and plywood due to changes of temperature.

Tension and compression tests were carried out, measurements of the elastic modulus being made only in the case of the tensile tests. The tests were carried out parallel, perpendicular, and at 45° to the grain of the outer veneers.

The tensile tests were carried out on specimens 12 inches long by 2 inches wide with a parallel portion $2\frac{1}{2}$ inches long and 1 inch wide at the centre, and parallel portions of full width 2 inches long at the ends, the connecting radius being about 12 inches. The deformations were determined by means of a Gerrard extensometer measuring over a 2-in. gauge length, and load deformation curves were plotted. The testing procedure was generally in accordance with the Australian Standard Specifications (8).

The compression tests were carried out on packs of specimens $3\frac{3}{4}$ inches long by 1 inch wide. The packs were made up into thicknesses of as near to an inch as possible in the case of 3/16 in. and $\frac{1}{4}$ in. plywood but this was not possible with the $\frac{1}{8}$ inch plywood as the sheets

were not of sufficient size to cut sixteen pieces in each direction and the pack was only half an inch thick in this case. These packs were held in a special end-clamping apparatus developed by Thomas (12). A number of types had been tried but this one was found to be the most satisfactory. The same rate of loading was adopted as in the tensile tests.

## 5. Results of Tests

The results which have been obtained by dividing the maximum load by the total cross section of the specimen have been averaged and the averages plotted in Figs. 1 to 9. Figs. 1 to 3 show the results for modulus of elasticity as measured in the tensile tests, Figs. 4 to 6 for maximum tensile strength, and Figs. 7 to 9 for maximum crushing strength. Curves have been fitted by the method of least squares to the points shown, the significance of the regressions being indicated in Table 1 where the actual regression factors are given. The regression lines have been fitted using a logarithmic transformation as the data vary somewhat exponentially with moisture content. The use of transformations has been discussed in a report by Williams (13). The regression factors are the factors by which the strength at a given initial moisture content must be multiplied for each 1 per cent. decrease in moisture content to determine the strength at the decreased moisture content. For $m$ per cent. decrease in moisture content it is therefore necessary to multiply by the $m$th power of the regression factor. That is, if $r$ is the regression factor and $S_n$ the strength or elastic modulus at a moisture content $n$, then the value $S_{(n+m)}$ at a moisture content $(n + m)$ is given by

$$S_n = S_{(n+m)} r^m$$

This is seen to be of the same form as Wilson's exponential formula (14) since on expressing the above formula in the exponential form it becomes

$$S_n = S_{(n+m)} e^{m \log r}$$

which is identical with Wilson's formula when $\log 1/r$ is replaced by $K$. In the case of an increase in moisture content the strength value is divided instead of multiplied by the repression factor.

Since additive corrections cannot be made, Tables 2 to 4 have been computed giving the strength and elastic modulus at each integral percentage throughout the range of moisture content values covered by the experiment. In both figures and tables the direction of grain refers to that of the outer veneers relative to the loading axis of the specimen.

## 6. Discussion of Results

In some cases the results do not differ significantly from a linear relationship and an additive correction could be used. This can be seen from the fitted curves in Figs. 1 to 9. Such corrections have, however, not been given. Generally, the maximum crushing strength shows little difference in regression factors for different thicknesses or glues but the linear regressions on moisture content are always significant. Often the regression deviates significantly from the linear, especially for specimens cut at 45° to the direction of the grain. The moisture corrections themselves also vary considerably, for different grain directions, and somewhat for glues and occasionally thicknesses.

In the case of maximum tensile strength, the regression was not significant in eight of the 27 tests, whilst in two others the signficance was only at the 5 per cent. level of probability. Seven of the fifteen highly significant regressions also deviate significantly from linearity whilst two have no significant linear trend but have a quadratic term which is significant. In specimens tested parallel to the grain, the trends vary, the corrections being greatest for phenol-formaldehyde glue and least for casein. For specimens tested perpendicular to the grain, the regression is significant for all thicknesses with urea-formaldehyde glue, and these are the only ones for which the property increases with increasing moisture content. In no case is it significant for casein glue and only with $\frac{1}{8}$-in. plywood for phenol-formaldehyde glue. For specimens tested at 45° to the grain, the corrections are rather variable and, in six cases, the regressions are curvilinear, the linear regression being non-significant for two of the cases where the quadratic term is significant.

All but one of the corrections for modulus of elasticity in tension parallel to the grain of the outer veneers, are significant, the regressions being linear. The corrections here do not differ significantly between types of glue or thicknesses although they do between directions of grain. For tension perpendicular to the grain of the outer veneers, the corrections do not differ significantly amongst themselves and so may be averaged, whilst those for tests at 45° differ significantly for different types of glue.

Where the corrections do not differ significantly between glues, thicknesses or direction of grain, average corrections could have been given. Strength figures, expressed as a percentage of the strength at 12 per cent. moisture content, have instead been tabulated for each integral percentage of moisture content throughout the range of the observations, for each glue, thickness and direction of grain.

In a recent unpublished report by Sulzberger (11), comparable values are to be found, although these apply only to one thickness of plywood, namely 3/16-in. three-ply, and to only one glue, namely urea-formaldehyde. For tensile strength, his results are a few per cent. higher parallel and perpendicular to the grain, but do not differ appreciably from the present ones at 45° to the grain. For modulus of elasticity, the same is true, except that at 45° to the grain a slight difference is apparent. The agreement is considerably closer for compressive strength parallel to the grain, although here again the results for tests at 45° to the grain differ slightly. This is illustrated in Fig. 10 for compressive strength.

### 7. Comparison with Solid Timber

No completely satisfactory comparison is possible between the variation of the strength of plywood and of solid timber with moisture content, as the values for the former vary so greatly amongst themselves. Expressed as regression factors, the moisture corrections for solid hoop pine are as follows (6):—

1·012 for tension parallel to the grain;
1·047 for compression parallel to the grain;
1·025 and 1·027 for compression perpendicular to the grain for the load applied to the tangential and radial faces respectively; and
1·019 for modulus of elasticity (tensile test).

TABLE 1.—REGRESSION FACTORS OF STRENGTH PROPERTIES AND ELASTIC MODULUS OF HOOP PINE PLYWOOD ON MOISTURE CONTENT

| Property | Direction of Grain of Face Veneer | Regression Factor. | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | Phenol-Formaldehyde Glue | | | Urea-Formaldehyde Glue | | | Casein Glue | | |
| | | ⅛ in. Plywood | 5/32 in. Plywood | ¼ in. Plywood | ⅛ in. Plywood | 5/32 in. Plywood | ¼ in. Plywood | ⅛ in. Plywood | 5/32 in. Plywood | ¼ in. Plywood |
| Maximum Crushing Strength | Parallel .. | 1·058** | 1·062** | 1·060** | 1·063** | 1·059**C. | 1·053** | 1·057** | 1·059** | 1·057** |
| | Perpendicular .. | 1·060** | 1·068** | 1·067** | 1·062** | 1·071**C. | 1·059** | 1·062** | 1·062** | 1·062**C. |
| | 45° .. .. | 1·054**C. | 1·046**C. | 1·045** | 1·042** | 1·046**C. | 1·023** | 1·047**C. | 1·046**C. | 1·040**C. |
| Maximum Tensile Strength | Parallel .. | 1·026**C. | 1·016**C. | 1·016 N.S. | 1·005 N.S. | 1·012** | 1·020**C. | 1·001 N.S. | 1·012** | 1·017** |
| | Perpendicular .. | 1·014* | 1·005 N.S. | 1·007 N.S. | ·975** | ·984** | ·978** | 1·001 N.S. | 1·001 N.S. | 1·004 N.S. |
| | 45° .. .. | 1·017** | 1·012** | 1·004 N.S. C. | 1·011**C. | 1·005* | ·998 N.S. C. | 1·016**C. | 1·017**C. | 1·008**C. |
| Modulus of Elasticity | Parallel .. | 1·026** | 1·011** | 1·018** | 1·013** | 1·010** | 1·026** | 1·016** | 1·015** | 1·007 N.S. |
| | Perpendicular .. | 1·021** | 1·013* | 1·008 N.S. | 1·009* | 1·015** | 1·011 N.S. | 1·013** | 1·015** | 1·013** |
| | 45° .. .. | 1·040** | 1·045**C. | 1·043** | 1·036** | 1·030**C. | 1·022** | 1·040** | 1·028**C. | 1·038** |

** Significant at the 1 per cent. level of probability.
* Significant at the 5 per cent. level of probability.
C. Regression departs significantly from the linear at the 1 per cent. level of probability.
N.S. No significant linear regression.
For an increase of 1 per cent. moisture content, divide by the regression factor.

TABLE 2.—TENSILE MODULUS OF ELASTICITY OF HOOP PINE PLYWOOD AT VARIOUS MOISTURE CONTENTS

(*Expressed as a percentage of the value at 12 per cent. moisture content*)

| Glue | Percentage Moisture Content | Parallel to the Grain | | | Perpendicular to the Grain | | | At 45° to the Grain | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | ¼ in. Plywood | ⅜ in. Plywood | ½ in. Plywood | ¼ in. Plywood | ⅜ in. Plywood | ½ in. Plywood | ¼ in. Plywood | ⅜ in. Plywood | ½ in. Plywood |
| Phenol-formaldehyde | 6 | 116 | 107 | 111 | 113 | 108 | 105 | 126 | 130 | 129 |
| | 7 | 114 | 106 | 109 | 111 | 107 | 104 | 122 | 124 | 124 |
| | 8 | 111 | 104 | 108 | 109 | 105 | 103 | 117 | 119 | 118 |
| | 9 | 108 | 103 | 106 | 106 | 104 | 102 | 113 | 114 | 114 |
| | 10 | 105 | 102 | 104 | 104 | 103 | 102 | 108 | 109 | 109 |
| | 11 | 103 | 101 | 102 | 102 | 101 | 101 | 104 | 104 | 104 |
| | 12 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| | 13 | 97 | 99 | 99 | 98 | 99 | 99 | 96 | 96 | 96 |
| | 14 | 95 | 98 | 97 | 96 | 98 | 98 | 92 | 92 | 92 |
| | 15 | 93 | 97 | 95 | 94 | 96 | 98 | 89 | 88 | 88 |
| | 16 | 90 | 95 | 93 | 92 | 95 | 97 | 85 | 84 | 85 |
| | 17 | 88 | 95 | 92 | 90 | 94 | 96 | 82 | 80 | 81 |
| Urea-formaldehyde | 6 | 108 | 106 | 117 | 105 | 109 | 107 | 124 | 119 | 114 |
| | 7 | 107 | 105 | 114 | 104 | 108 | 106 | 119 | 116 | 112 |
| | 8 | 105 | 104 | 111 | 104 | 106 | 104 | 115 | 112 | 109 |
| | 9 | 104 | 103 | 108 | 103 | 105 | 103 | 111 | 109 | 107 |
| | 10 | 103 | 102 | 105 | 102 | 103 | 102 | 107 | 106 | 105 |
| | 11 | 101 | 101 | 103 | 101 | 102 | 101 | 103 | 103 | 102 |
| | 12 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| | 13 | 99 | 99 | 97 | 99 | 99 | 99 | 97 | 97 | 98 |
| | 14 | 98 | 98 | 95 | 98 | 97 | 98 | 93 | 94 | 96 |
| | 15 | 96 | 97 | 93 | 97 | 96 | 97 | 90 | 92 | 94 |
| | 16 | 95 | 96 | 90 | 96 | 94 | 96 | 87 | 89 | 92 |
| | 17 | 94 | 95 | 88 | 96 | 93 | 95 | 84 | 86 | 90 |
| | 18 | 93 | 94 | 86 | 95 | 92 | 94 | 81 | 84 | 88 |
| | 19 | 92 | 93 | 84 | 94 | 90 | 93 | 78 | 81 | 86 |
| Casein .. .. | 8 | 106 | 106 | 103 | 106 | 106 | 105 | 117 | 112 | 116 |
| | 9 | 105 | 104 | 102 | 104 | 105 | 104 | 113 | 109 | 112 |
| | 10 | 103 | 103 | 102 | 103 | 103 | 103 | 108 | 106 | 108 |
| | 11 | 101 | 101 | 101 | 101 | 102 | 101 | 104 | 103 | 104 |
| | 12 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| | 13 | 98 | 99 | 99 | 98 | 98 | 99 | 96 | 98 | 96 |
| | 14 | 97 | 96 | 98 | 96 | 97 | 98 | 92 | 95 | 93 |
| | 15 | 95 | 95 | 98 | 96 | 96 | 96 | 89 | 92 | 90 |
| | 16 | 93 | 94 | 97 | 95 | 94 | 95 | 86 | 90 | 86 |
| | 17 | 92 | 92 | 96 | 94 | 93 | 94 | 82 | 87 | 83 |

| Glue | Percentage Moisture Content | Tension Perpendicular to the Grain | | | Tension Perpendicular to the Grain | | | Tension Perpendicular to the Grain | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | ⅛ in. Plywood | 3/16 in. Plywood | ¼ in. Plywood | ⅛ in. Plywood | 3/16 in. Plywood | ¼ in. Plywood | ⅛ in. Plywood | 3/16 in. Plywood | ¼ in. Plywood |
| Phenol-formaldehyde | 6 | 117 | 110 | 111 | 109 | 103 | 104 | 111 | 108 | 103 |
| | 7 | 113 | 108 | 109 | 107 | 103 | 104 | 109 | 106 | 102 |
| | 8 | 111 | 106 | 107 | 106 | 102 | 103 | 107 | 105 | 102 |
| | 9 | 108 | 105 | 105 | 104 | 102 | 102 | 105 | 104 | 101 |
| | 10 | 105 | 103 | 104 | 103 | 101 | 101 | 103 | 103 | 101 |
| | 11 | 103 | 102 | 102 | 101 | 100 | 101 | 102 | 101 | 100 |
| | 12 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| | 13 | 98 | 98 | 99 | 99 | 100 | 99 | 98 | 99 | 100 |
| | 14 | 95 | 96 | 97 | 97 | 99 | 99 | 97 | 98 | 99 |
| | 15 | 92 | 96 | 96 | 96 | 98 | 98 | 95 | 97 | 99 |
| | 16 | 90 | 94 | 94 | 94 | 98 | 97 | 93 | 96 | 98 |
| | 17 | 88 | 92 | 92 | 93 | 97 | 96 | 92 | 94 | 98 |
| Urea-formaldehyde | 6 | 103 | 107 | 112 | 86 | 91 | 88 | 107 | 103 | 98 |
| | 7 | 103 | 106 | 109 | 88 | 92 | 90 | 105 | 102 | 99 |
| | 8 | 102 | 105 | 108 | 90 | 94 | 91 | 104 | 102 | 99 |
| | 9 | 102 | 104 | 106 | 93 | 95 | 94 | 103 | 101 | 100 |
| | 10 | 101 | 103 | 104 | 95 | 97 | 96 | 102 | 101 | 100 |
| | 11 | 101 | 101 | 102 | 98 | 98 | 98 | 101 | 100 | 100 |
| | 12 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| | 13 | 99 | 99 | 98 | 103 | 102 | 102 | 99 | 99 | 100 |
| | 14 | 99 | 97 | 96 | 105 | 103 | 104 | 98 | 99 | 101 |
| | 15 | 98 | 96 | 94 | 108 | 105 | 107 | 97 | 98 | 101 |
| | 16 | 98 | 96 | 92 | 111 | 107 | 109 | 96 | 98 | 101 |
| | 17 | 97 | 95 | 90 | 114 | 108 | 112 | 95 | 97 | 101 |
| | 18 | 97 | 93 | 88 | 117 | 110 | 114 | 94 | 97 | 101 |
| | 19 | 96 | 92 | 87 | 120 | 112 | 118 | 93 | 96 | 101 |
| Casein .. .. | 8 | 101 | 105 | 107 | 100 | 100 | 102 | 107 | 107 | 103 |
| | 9 | 101 | 104 | 105 | 100 | 100 | 101 | 105 | 105 | 102 |
| | 10 | 100 | 102 | 103 | 100 | 100 | 101 | 103 | 103 | 102 |
| | 11 | 100 | 101 | 101 | 100 | 100 | 100 | 101 | 102 | 101 |
| | 12 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| | 13 | 100 | 99 | 98 | 100 | 100 | 100 | 98 | 98 | 99 |
| | 14 | 100 | 97 | 97 | 100 | 100 | 99 | 97 | 97 | 98 |
| | 15 | 100 | 96 | 95 | 100 | 100 | 99 | 95 | 95 | 97 |
| | 16 | 100 | 95 | 94 | 100 | 99 | 98 | 94 | 94 | 96 |
| | 17 | 100 | 94 | 92 | 99 | 99 | 98 | 92 | 92 | 96 |
| | 18 | 100 | 93 | 90 | 99 | 99 | 98 | 91 | 90 | 95 |
| | 19 | 99 | 92 | 89 | 99 | 99 | 97 | 89 | 89 | 94 |
| | 20 | 99 | 91 | 87 | 99 | 99 | 97 | 88 | 88 | 94 |

TABLE 4.—MAXIMUM CRUSHING STRENGTH OF HOOP PINE PLYWOOD AT VARIOUS MOISTURE CONTENTS

*(Expressed as a percentage of the value at 12 per cent. moisture content)*

| Glue | Percentage Moisture Content | Compression Parallel to the Grain | | | Compression Perpendicular to the Grain | | | Compression at 45° to the Grain | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | ¼ in. Plywood | ⅜ in. Plywood | ½ in. Plywood | ¼ in. Plywood | ⅜ in. Plywood | ½ in. Plywood | ¼ in. Plywood | ⅜ in. Plywood | ½ in. Plywood |
| Phenol-formaldehyde | 6 | 140 | 144 | 142 | 142 | 148 | 148 | 137 | 131 | 130 |
| | 7 | 132 | 135 | 134 | 134 | 139 | 139 | 130 | 125 | 124 |
| | 8 | 125 | 127 | 126 | 126 | 130 | 130 | 122 | 120 | 119 |
| | 9 | 118 | 120 | 119 | 119 | 122 | 122 | 117 | 114 | 114 |
| | 10 | 112 | 113 | 112 | 112 | 114 | 114 | 111 | 109 | 109 |
| | 11 | 106 | 106 | 106 | 106 | 107 | 107 | 106 | 105 | 104 |
| | 12 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| | 13 | 95 | 94 | 94 | 94 | 94 | 94 | 95 | 96 | 96 |
| | 14 | 89 | 89 | 89 | 89 | 88 | 88 | 90 | 91 | 91 |
| | 15 | 84 | 83 | 84 | 84 | 82 | 82 | 86 | 87 | 87 |
| | 16 | 80 | 79 | 79 | 79 | 77 | 77 | 81 | 84 | 84 |
| | 17 | 75 | 74 | 75 | 75 | 72 | 72 | 77 | 80 | 80 |
| Urea-formaldehyde | 6 | 145 | 141 | 136 | 144 | 151 | 141 | 128 | 131 | 115 |
| | 7 | 136 | 133 | 129 | 135 | 141 | 133 | 123 | 125 | 112 |
| | 8 | 128 | 126 | 123 | 127 | 131 | 126 | 118 | 120 | 110 |
| | 9 | 120 | 119 | 117 | 120 | 123 | 119 | 113 | 115 | 107 |
| | 10 | 113 | 112 | 111 | 113 | 115 | 112 | 108 | 110 | 105 |
| | 11 | 106 | 106 | 105 | 106 | 107 | 106 | 104 | 105 | 102 |
| | 12 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| | 13 | 94 | 94 | 95 | 94 | 93 | 94 | 96 | 96 | 98 |
| | 14 | 88 | 89 | 90 | 89 | 87 | 89 | 92 | 91 | 96 |
| | 15 | 83 | 84 | 86 | 83 | 82 | 84 | 88 | 88 | 93 |
| | 16 | 78 | 79 | 81 | 79 | 76 | 80 | 85 | 84 | 92 |
| | 17 | 74 | 75 | 77 | 74 | 71 | 75 | 81 | 80 | 89 |
| | 18 | 69 | 71 | 73 | 70 | 66 | 71 | 78 | 76 | 87 |
| | 19 | 65 | 67 | 70 | 66 | 62 | 67 | 75 | 73 | 85 |
| Casein .. .. | 8 | 125 | 126 | 125 | 127 | 127 | 127 | 120 | 120 | .. |
| | 9 | 118 | 119 | 118 | 120 | 120 | 120 | 115 | 115 | 112 |
| | 10 | 112 | 113 | 112 | 114 | 113 | 113 | 110 | 110 | 108 |
| | 11 | 106 | 106 | 106 | 106 | 106 | 106 | 105 | 105 | 104 |
| | 12 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| | 13 | 95 | 94 | 95 | 94 | 94 | 94 | 95 | 96 | 96 |
| | 14 | 89 | 89 | 90 | 89 | 89 | 89 | 91 | 92 | 92 |
| | 15 | 85 | 84 | 85 | 84 | 83 | 83 | 87 | 88 | 89 |
| | 16 | 80 | 80 | 80 | 78 | 79 | 79 | 83 | 84 | 86 |
| | 17 | 76 | 75 | 76 | 74 | 74 | 74 | 80 | 80 | 82 |

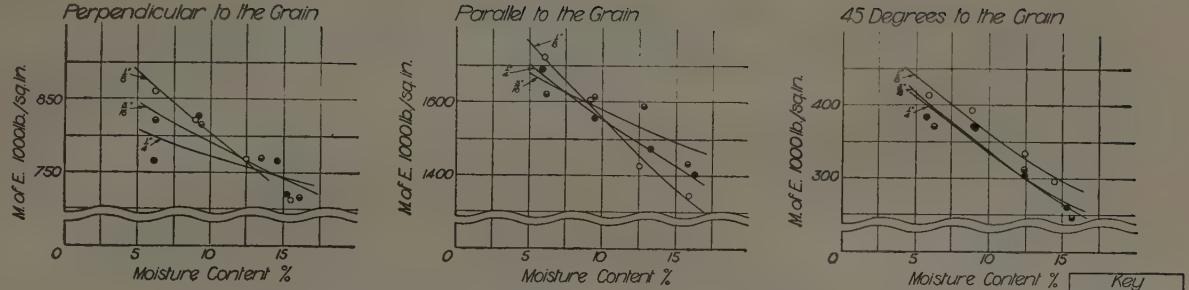


Fig. 1 Variation of Modulus of Elasticity with Moisture Content for Phenol-Formaldehyde bonded Plywood.

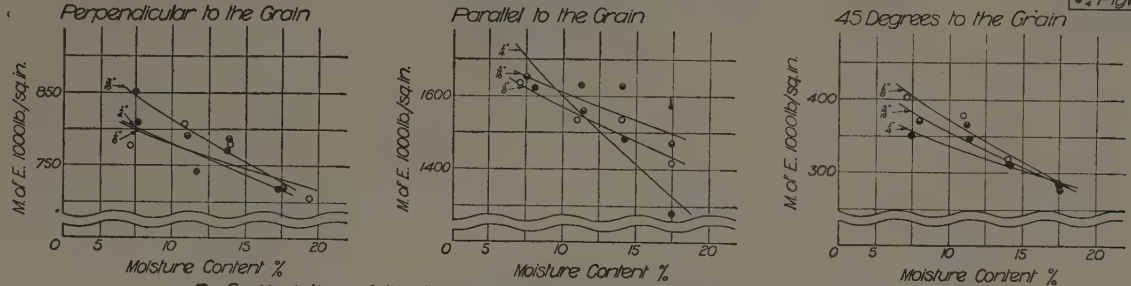


Fig. 2 Variation of Modulus of Elasticity with Moisture Content for Urea-Formaldehyde bonded Plywood.

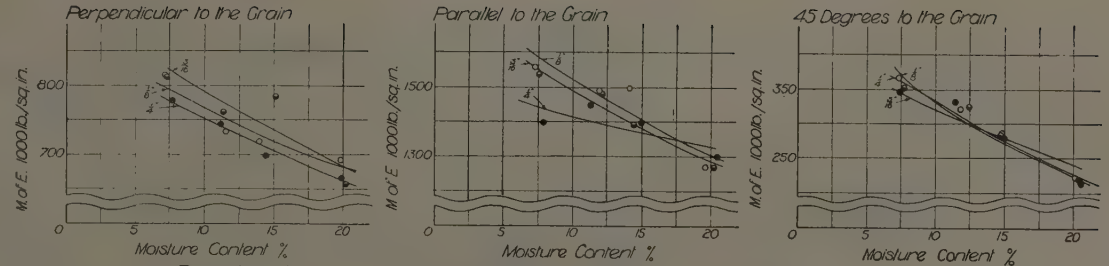


Fig. 3 Variation of Modulus of Elasticity with Moisture Content for Casein bonded Plywood.

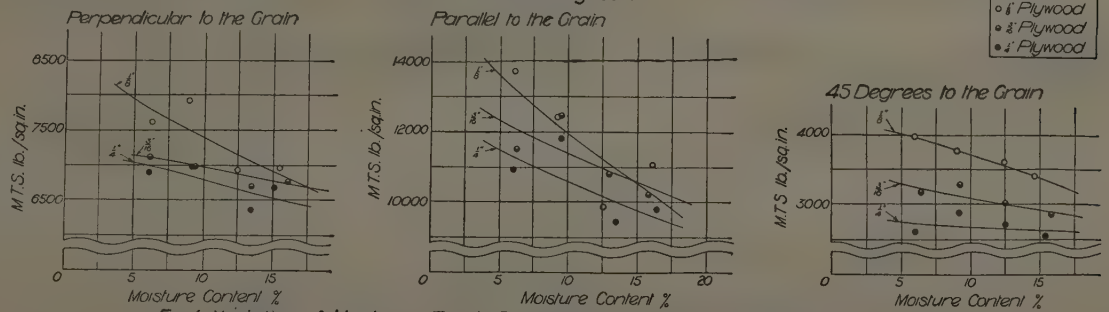


Fig. 4 Variation of Maximum Tensile Strength with Moisture Content for Phenol-Formaldehyde bonded Plywood.

Fig.5 Variation of Maximum Tensile Strength with Moisture Content for Urea-Formaldehyde bonded Plywood.

Fig.6 Variation of Maximum Tensile Strength with Moisture Content for Casein bonded Plywood.

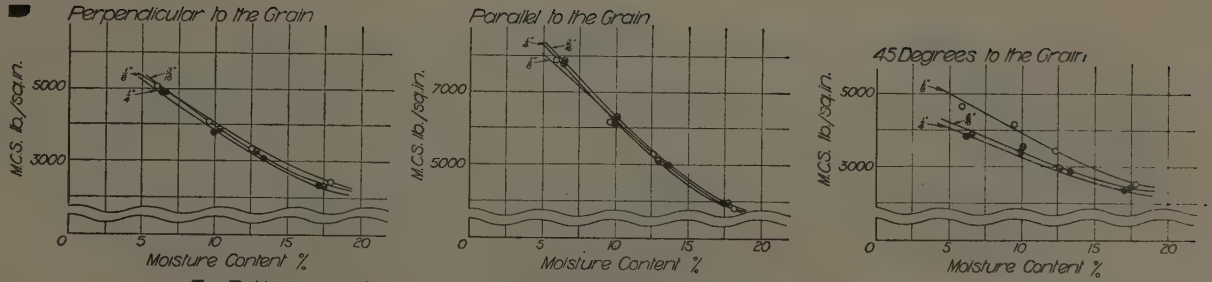


Fig. 7 Variation of Maximum Crushing Strength with Moisture Content for Phenol-Formaldehyde bonded Plywood.

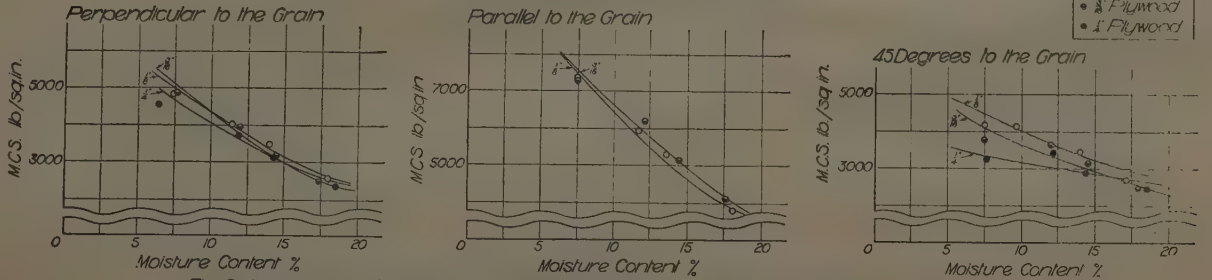


Fig. 8 Variation of Maximum Crushing Strength with Moisture Content for Urea-Formaldehyde bonded Plywood.

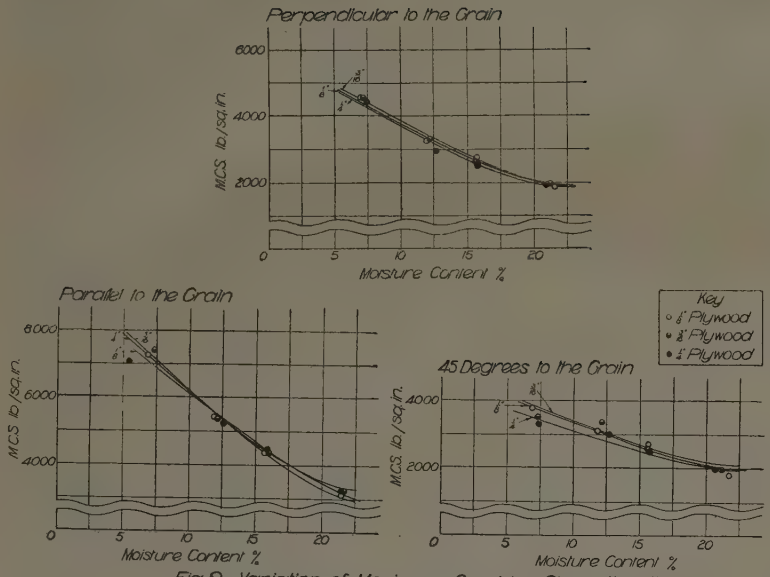


Fig. 9 Variation of Maximum Crushing Strength with Moisture Content for Casein bonded Plywood.

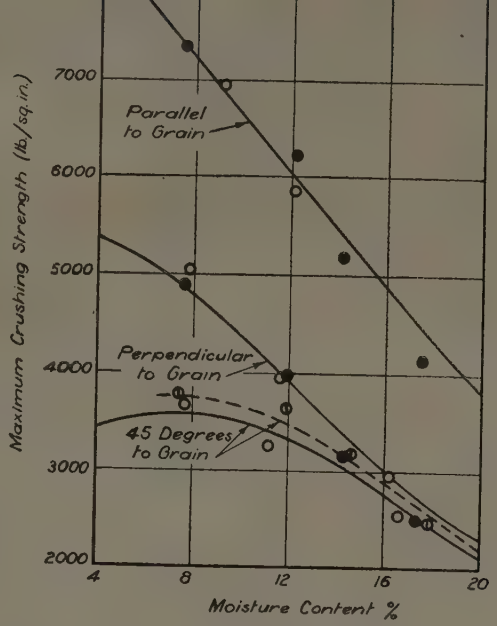


Fig.10. Comparison of Results Obtained by Sulzberger and the Author for the Effect of Moisture Content on Maximum Crushing Strength of Hoop Pine Plywood at 20°C.

Sulzberger □

Author { Parallel and Perpendicular ●
45 Degree to Grain ⊖

The above regression factors for solid timber were determined by expressing the additive moisture corrections as a fraction of the mean in each case and adding the results to unity, in agreement with the convention adopted here, since these regression coefficients for solid timber are all negative.

The corrections for plywood are of the same order of magnitude as those for solid timber where rough comparisons can be made, except for maximum crushing strength, parallel and perpendicular to the grain. Here the regression factors are in general somewhat higher than those for solid timber either parallel or perpendicular to the grain. However, in view of the fact that there is no great difference between the regression coefficients for plywood and solid timber, values predicted from corrections for solid timber could be used for plywood of other species until actual corrections for plywood of those species are available. This general agreement has also been observed for Douglas fir and Sitka spruce (1).

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# The Extraction of Lignin from *Eucalyptus regnans* F.v.M. by Means of Methanol

*By D. E. Bland, M.Sc.,* E. A. Hanson, Dr.Phil.,† C. M. Stewart, B.Sc.,‡ and A. J. Watson, A.M.T.C.**

*Summary*

A survey of possible methods of extracting native lignin from immature *Eucalyptus regnans* F.v.M. led to the conclusion that one of the most promising solvents was methanol. Treatment with this solvent for 24 hours at 150°C removed a little more than one quarter of the lignin, estimated as Klason lignin, present in a specimen of *E. regnans* sapwood sawdust. Treatment for 148 hours, using fresh methanol every sixteen hours, removed about 70 per cent. of the original lignin estimated as Klason lignin. Evidence was obtained to show that the methanol extraction of wood is essentially a mild acid hydrolysis accompanied by the solvent action of methanol. During the process some of the extracted lignin was degraded to materials soluble in water and ether. The remainder could be precipitated as a buff powder which gave the colour reactions of native lignin and which was soluble in bisulphite solutions.

## 1. Introduction

Lignin has not been obtained as a pure substance and has therefore not been characterized by definite physical constants and chemical properties, nor is there any concise definition of lignin. It is known, however, to be a biological material readily denatured by extraction processes. When obtained as a by-product from the wood pulp industry it is extensively degraded and differs widely in its properties from the lignin as it occurs in wood. Methods of isolation involving the destruction of the cellulose by concentrated acids give lignins which are highly polymerized and non-reactive. Klason lignin, isolated from wood or pulp by means of 72 per cent. sulphuric acid, is widely recognized provisionally as a measure of the lignin content.

Aronovsky and Gortner (1936) pulped aspen wood with aqueous alcohols and found that butanol was the most effective, reducing the lignin content of the pulp to 3 per cent. It was suggested that the ligneous material so obtained was less denatured than lignins obtained by inorganic reagents. Bailey (1940) found that the lignin was almost completely removed from aspen wood by cooking with butanol and water. The removal was greatly accelerated by the presence of 2 per cent. sodium hydroxide, which he considered to act as a catalyst. He noticed that, with neutral butanol cooks, the cooking liquor became acid.

Charbonnier (1942) found that neutral butanol and water extracted only a small part of the lignin from aspen wood. He was thus unable to confirm the observations of Bailey on the pulping qualities of butanol. He found it necessary to add sodium hydroxide, as Bailey had in most of his experiments, and considered that the lignin thus obtained was not a native lignin but a typical alkali lignin.

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Hewson, McCarthy, and Hibbert (1941) were able to remove somewhat less than half of the lignin from maple wood by extraction with ethanol for four hours at 200°C. This produced, besides ethanol lignin, "lignin tar" and some distillable oils. They considered that the drastic conditions necessary indicated that the lignin units were in combination in the wood as ethanol-insoluble aggregates.

Overbeck and Müller (1942) cooked various woods with water at temperatures ranging from 130° to 165°C. They found that some of the wood substance was dissolved and that part of the lignin became soluble in alcohol. They also noticed that the cooking liquor became acid and concluded that the process was essentially an acid hydrolysis. The residual lignin in the wood was somewhat more resistant to sulphite cooking than the original lignin.

Katzen, Sawyer, and Othmer (1945) showed that lignin solubility decreased with increase in the number of carbon atoms in monohydric alcohols.

Brauns (1939) extracted spruce wood with water and ether and then with alcohol at room temperature. On concentrating the alcoholic solution and pouring into distilled water, a creamy precipitate was obtained which gave all the reactions of native lignin. It constituted, however, only a small part of the total lignin in the wood.

No work has yet been reported on the native lignin of eucalypts.

## 2. Outline of Experimental Procedure

### (i) *Preparation of the Wood Sample*

Immature trees of *Eucalyptus regnans* F.v.M. ranging in age from six to ten years and free from truewood, were selected. Truewood was avoided because it was considered that the more severe extraction conditions necessary for the removal of the extraneous materials might remove some lignin. The logs were cut into short lengths, the bark removed, gum veins, pockets, and knots sawn out, and the remaining clear wood reduced to sawdust. In the first experiments, the sawdust was washed with water and then dried by repeated washing at room temperature with dry methanol. Later, it was found that the extraction of the lignin was not appreciably affected by oven-drying the sawdust. For most of the experiments, therefore, the wood was washed three times with cold water, three times with hot water, air-dried and then oven-dried. Alcohol treatment was not given as it was considered that it might remove some of the native lignin described by Brauns. Later experiments showed that the amount of lignin thus removed was negligible.

### (ii) *Preliminary Extraction Experiments*

Some pilot experiments with lower monohydric alcohols showed that methanol was the most effective lignin extractant. As the introduction of alkoxyl groups other than methoxyl would complicate the methoxyl determination, and since methanol could very much more easily be evaporated from the wood than could a higher alcohol, it was decided to investigate thoroughly the action of methanol. The drying of methanol-wet wood was accordingly investigated. Following this, extractions were carried out at temperatures ranging from 60° to

160°C. with the following solvents: (i) methanol, (ii) methanol plus 0·4 per cent. water, (iii) methanol plus 2·0 per cent. dry hydrogen chloride, (iv) methanol plus 0·4 per cent. water plus 2·0 per cent. dry hydrogen chloride. Under the same conditions, increasing amounts of lignin were removed by the solvents in the order enumerated. The time factor was also important, more lignin being extracted with longer periods of time up to 160 hours. Methanol at 160°C. caused the residual wood to have a slightly charred appearance, whereas methanol containing 0·4 per cent. water and methanol containing 2·0 per cent. hydrogen chloride produced wood residues with colours close to that of the original sawdust. The methanol-hydrogen chloride, besides removing more lignin than did dry methanol, also dissolved a considerable amount of the carbohydrate material. The solvents containing water produced a dark red lignin, whereas that obtained with dry solvent was buff coloured. Since methanol appeared to dissolve the lignin more specifically than did the other solvents, its action was further investigated.

(iii) *Methanol Extractions*

Extractions of oven-dry wood with methanol at 150°C were carried out for various times. Mild steel bombs containing 150 ml. of methanol, 6·0 g. of dry sawdust, and with about 20 ml. of air space, were tumbled in a thermostatically controlled oil bath for the required time. Later, extractions of 1 kg. of sawdust with 12 l. of methanol were carried out in a mechanically-stirred, stainless steel autoclave. Each charge was subjected to one 4-hour and then nine 16-hour extractions, with fresh methanol used for each extraction. The amounts of Klason lignin and ester in the methanol were estimated for each extraction.

The total material removed was estimated from the loss of weight of the wood sample after extraction, drying and weighing. The total weight of extract was determined by evaporating an aliquot portion of the methanol solution to dryness on the water bath. In later experiments the extract was analysed for precipitated lignin, Klason lignin and esters. The wood residues were analysed for holocellulose, Cross and Bevan cellulose, pentosans, Klason lignin, and methoxyl. The methanol solutions were concentrated and methods of precipitating the lignin were investigated. The existence of water-soluble materials giving lignin reactions was demonstrated. The precipitated lignins and Klason lignins from the residual woods were analysed for methoxyl and the methoxyl not in Klason lignin was calculated for the original wood and for the methanol extracted woods.

(iv) *Methanol-HCl Extractions*

After the methanol extraction, the residual wood was treated for different periods with boiling methanol containing 2·0 per cent. dry hydrogen chloride. The residues were analysed as before.

(v) *Investigation of the Action of Methanol*

The action of methanol on acetic acid and on certain sugars in the presence of acetic acid was investigated. Methanol recovered from the large scale extractions was examined for the presence of acids and esters.

### 3. Results and Discussions

The drying of alcohol-wet wood powders proved to be difficult. This was to be expected after the observation of Cohen (1936) that wood powders retain a certain amount of ethanol. A one gram water-wet sample of *E. regnans* wood meal took about 1½ hours to dry at 100°C. A methanol-wet sample of the same size took about three times as long at the same temperature, notwithstanding the higher volatility of the methanol. This difficulty was more marked with ethanol and very much more with butanol. During the drying of sawdust wet with methanol a distinct odour of formaldehyde was noted. Exhaustive washing of oven-dried methanol-extracted wood samples with ether did not appreciably reduce the methoxyl content; it appears from this that the methanol may not have been retained as such.

The amounts of material removed by methanol extraction under different conditions are shown in Tables 1, 2, and 3. It appears from the results in Table 1 that the total material removed was greater than

TABLE 1.—RESULTS OF EXTRACTION OF 60-80 MESH *E. regnans* WITH DRY METHANOL FOR 24 HOURS AT DIFFERENT TEMPERATURES

| Temperature (Deg. C.) | Total Material Removed* | Klason Lignin Removed* |
|---|---|---|
| 60 | 0·9 | 2·5 |
| 110 | 3·5 | 3·2 |
| 160 | 21·0 | 15·5 |

* All results expressed as percentages of the original wood. Original wood 21·9 per cent. Klason lignin.

the total amount of lignin removed, and from Table 2 that the total amount of material removed from the wood was greater than the total weight of extract obtained on evaporation of the methanol. This was in turn greater than the total Klason lignin extracted, which again was greater than the amount of lignin recovered by precipitation. The excess total material removed over the weight of extract became progressively greater with time and may have been due to loss of volatile materials during evaporation. The result at 60°C, given in Table 1, is apparently inconsistent in that the total extractives were less than the amount of Klason lignin lost. This is probably due, however, to the very small amount of material extracted and therefore the large influence of the error of drying methanol-wet wood.

In the first experiments, precipitation of the lignin was carried out by pouring the concentrated methanol solution into distilled water; this caused some of the lignin to go into colloidal solution, only a variable and indefinite fraction being precipitated. An electrophoresis experiment showed that the lignin was present as a negatively-charged colloid. It was found that the water-insoluble lignin could be precipitated by making the solution alkaline with sodium hydroxide and then adding hydrochloric acid until the solution was decinormal in acid. This procedure brought down the lignin as a buff-coloured precipitate.

It could also be precipitated by the addition of salts. The filtrate from the precipitation of the lignin reduced Fehling's solution only very feebly, even after boiling with hydrochloric acid, and it was also negative to Molisch's reagent. Lignin reactions, however, both with chlorine and sodium sulphite and with phloroglucinol, were strongly positive. Repeated extraction of this filtrate with benzene or ether finally made the aqueous layer negative to the phloroglucinol test and only feebly positive to the chlorine and sodium sulphite test. On evaporation of the combined benzene or ether extracts, a sticky resinous material giving strong lignin reactions was obtained.

It can be seen from Table 2 that the rate of removal of lignin estimated as Klason lignin decreased rapidly with time. After treatment for four days the water-solubility of the wood meal had increased from 1·0 to 7·2 per cent., and the alkali-solubility had increased from 9·7 to 17·3 per cent. of the weight of the original wood.

TABLE 2.—RESULTS OF EXTRACTION OF OVEN-DRY *E. regnans* SAWDUST WITH DRY METHANOL AT 150°C. FOR VARIOUS TIMES

| Duration of Extraction | Total Material Removed | Weight of Extract | Weight of Precipitated Lignin | Klason Lignin Extracted |
|---|---|---|---|---|
| 4 hours .. .. | 5·4 | 5·3 | 4·0 | 2·8 |
| 1 day .. .. | 14·1 | 13·1 | 8·3 | 9·3 |
| 2 days .. .. | 19·4 | 17·7 | 11·2 | 11·5 |
| 4 days .. .. | 24·5 | 22·4 | 9·0 | 14·6 |
| 6 days .. .. | 24·2 | 20·9 | 10·2 | 14·6 |

All results expressed as percentages of the original wood. Original wood 22·6 per cent. Klason lignin.

The results of the extraction of 1 kg. of sawdust are shown in Table 3. The yield of Klason lignin from the extract was determined by treating the total solids, obtained on evaporation of the methanol, according to the Division of Forest Products standard method for lignin determination. It can be seen that the ratio of Klason lignin to methyl acetate, excluding the ratio for the preliminary four-hour extraction, increased from four to thirteen between the first and ninth sixteen-hour extractions.

The methoxyl contents of precipitated methanol lignins, of Klason lignin and of the residual wood are shown in Table 4. The methoxyl content of the methanol lignin (column 2) recovered from extractions lasting longer than four hours was practically constant at a value considerably higher than that for the Klason lignin either from the original wood or from any of the residual woods. The methoxyl in Klason lignin was calculated as a percentage of the original wood thus: after one day the Klason lignin content of the residual wood was 13·3 per cent. of the original wood. Hence $(22{\cdot}6 - 13{\cdot}3) = 9{\cdot}3$ per cent. of Klason lignin had been extracted. The residual Klason lignin contained 22·8 per cent. methoxyl and therefore the methoxyl in lignin as a percentage of the wood was 22·8 per cent. of $13{\cdot}3 = 3{\cdot}03$ per cent., whereas the total methoxyl content of the wood was 5·62 per cent., and therefore methoxyl not in Klason lignin constituted 2·59 per cent. of the wood.

The analyses of the original wood and of the wood after methanol extraction for different periods of time are shown in Table 5. Whereas, in the original wood, the sum of the percentages of lignin and holocellulose was close to 100, this was not so for the extracted woods,

TABLE 3.—LIGNIN AND ESTERS PRODUCED BY SUCCESSIVE METHANOL EXTRACTIONS OF *E. regnans* SAWDUST

| Extraction Time | Total Solids in Extract (*a*) | Klason Lignin in Extract (*b*) | Ratio *a/b* | Precipitable Lignin in Extract (*c*) | Esters as Methyl Acetate (*d*) | Ratio *b/d* | Methoxyl Content of Precipitated Lignin |
|---|---|---|---|---|---|---|---|
| 4 hr. .. .. | 2·95 | 2·32 | 1·27 | 1·15 | 0·25 | 9·3 | 18·7 |
| 1st 16 hr. .. | 4·42 | 3·19 | 1·38 | 1·42 | 0·74 | 4·3 | 24·1 |
| 2nd 16 hr. .. | 3·67 | 2·77 | 1·32 | 1·31 | 0·66 | 4·2 | 26·0 |
| 3rd 16 hr. .. | 2·93 | 2·21 | 1·33 | 1·13 | 0·41 | 5·4 | 26·0 |
| 4th 16 hr. .. | 2·28 | 1·70 | 1·34 | 0·94 | 0·25 | 6·8 | 25·6 |
| 5th 16 hr. .. | 1·68 | 1·25 | 1·34 | 0·73 | 0·14 | 8·9 | 26·7 |
| 6th 16 hr. .. | 1·33 | 0·94 | 1·41 | 0·55 | 0·10 | 9·4 | 26·3 |
| 7th 16 hr. .. | 1·10 | 0·74 | 1·49 | 0·42 | 0·08 | 9·3 | 25·4 |
| 8th 16 hr. .. | 0·95 | 0·58 | 1·64 | 0·35 | 0·06 | 9·7 | 26·2 |
| 9th 16 hr. .. | 0·85 | 0·53 | 1·60 | 0·30 | 0·04 | 13·2 | 26·5 |
| Total .. | .. | 16·23 | .. | 8·30 | 2·73 | .. | .. |

*a*, *b*, *c*, and *d*—percentage of original wood.

the discrepancy becoming more marked after the longer period of treatment. This must be due to portion of the carbohydrate fraction becoming soluble in the reagents used. Only two to four chlorinations and subsequent ammoniacal alcohol treatments were required to delignify the methanol-extracted samples in the holocellulose determination, whereas the original wood required eight. This, combined with the large increase in water-soluble material mentioned above, shows clearly that the carbohydrates of the wood were considerably modified by the methanol treatment.

TABLE 4.—METHOXYL CONTENTS OF ISOLATED LIGNINS AND RESIDUAL WOODS

| Duration of Extraction | Precipitated Methanol Lignin (Percentage Lignin) | Klason Lignin | | Total Methoxyl in Wood (Percentage) | Methoxyl not in Klason Lignin (Percentage Original Wood) |
|---|---|---|---|---|---|
| | | Percentage Lignin | Percentage Original Wood | | |
| 0 (Original wood) | .. | 22·6 | 5·11 | 7·48 | 2·37 |
| 4 hours .. | 26·5 | 23·6 | 4·67 | 6·97 | 2·30 |
| 1 day .. | 28·3 | 22·8 | 3·03 | 5·62 | 2·59 |
| 2 days .. | 28·6 | 21·9 | 2·43 | 4·55 | 2·12 |
| 4 days .. | 28·6 | 21·7 | 1·73 | 3·54 | 1·81 |
| 6 days .. | 28·7 | 22·0 | 1·76 | 3·54 | 1·78 |

Original wood 22·6 per cent. Klason lignin.

The results of the methanol-HCl extractions of the methanol-extracted wood residues are shown in Table 6. It is apparent that a further considerable quantity of lignin was rapidly taken into solution,

but that extension of the extraction time beyond four hours did not extract much more. In this case the ratio of the total amount of material extracted to the amount of recovered lignin (about 4 : 1) is greater than the corresponding ratio (about $2\frac{1}{2}$ : 1) for the methanol extraction. There remained in the wood a third fraction of the lignin which resisted even the methanol-HCl treatment.

TABLE 5.—ANALYSIS OF METHANOL EXTRACTED *E. regnans*
(*Per cent. oven-dry sample weight.*)

| Duration of Extraction | Lignin | Holocellulose | Lignin + Holocellulose |
|---|---|---|---|
| 0 (Original wood) .. .. | 24·0 | 75·4 | 99·4 |
| 4 hours .. .. .. | 21·3 | 73·8 | 95·1 |
| 4 hr. + 16 hr. (1) .. .. | 17·4 | 70·3 | 87·7 |
| 4 hr. + 16 hr. + methanol-HCl extraction (2) .. .. | 9·2 | 72·3 | 81·5 |

(1) After extraction for four hours again extracted for sixteen hours with fresh solvent.

(2) Residue from (1) given methanol-HCl extraction for four hours.

A wood sample and the residue from the same wood after 72 hours of methanol extraction were analysed and the results are given in Table 7. It can be seen that the holocellulose content of the residual wood was only 8 per cent. higher than the Cross and Bevan cellulose content, whereas in the original wood it was 22 per cent. higher. There was only a small loss of Cross and Bevan cellulose and more than half of this was accounted for by loss of xylan. Thus the true cellulose remained practically unaffected by the methanol extraction, whereas the hemicelluloses were largely affected so as to render them soluble in the holocellulose reagents. These results constitute yet further indication that it is not possible to remove lignin from the wood without affecting the carbohydrate portion, chiefly the hemicelluloses, and that rupture of the ligno-cellulose bond involves liberation of some of the hemicelluloses.

TABLE 6.—RESULTS OF METHANOL-HYDROCHLORIC ACID EXTRACTION OF METHANOL-EXTRACTED WOOD

| Duration of Extraction | Amount Extracted | Weight of Precipitated Lignin | Klason Lignin Content of Wood Residue |
|---|---|---|---|
| 0 .. .. .. | .. | .. | 10·30 |
| 5 mins. .. .. .. | 4·7 | 1·50 | 7·15 |
| 4 hours .. .. .. | 16·1 | 4·45 | 4·81 |
| 24 hours .. .. .. | 20·2 | 4·77 | 4·10 |

All results expressed as percentages of original wood.

The methanol recovered from successive sixteen-hour extractions of 1 kg. of wood was found to contain esters (estimated by saponification and calculated as methyl acetate) in amounts shown in Table 3. Total esters produced during nine successive sixteen-hour extractions

amounted to 2·73 per cent. of the weight of the original wood. The original wood contained 3·2 per cent. acetyl and the last residue 1·3 per cent.

Lignin is not extractable by cold methanol but, once the methanol lignin is obtained, it is freely soluble in cold methanol. This is a clear indication that this material is derived by the breakdown of some larger molecule such as a lignin carbohydrate compound.

When 1 g. of acetic acid was heated in 150 ml. of methanol at 150°C. for 16 hours, it was found to be almost completely esterified. This does not exclude the possibility that acid conditions obtained throughout the extraction, because acidity could be maintained by slow liberation of acid from the wood. It can be seen from Table 3 that the ratio of Klason lignin extracted to total material extracted was roughly constant. From the ratio of Klason lignin in extract to methyl acetate formed, it appears that the formation of methyl acetate took place concurrently with the lignin removal, greater amounts of the ester being formed per unit amount of lignin as the extraction proceeded. This may be interpreted as showing that the methanol extraction is a mild acid hydrolysis. From the fact that the non-lignin extractives became larger in amount and reducing sugars were detectable in the liquor, it may be concluded that the further solution of lignin accomplished by methanolysis was accompanied by the hydrolysis of carbohydrate material. It appears, therefore, that the weakly acid methanol extraction opens the ligno-cellulose bond and removes lignin more specifically than do acid extractions.

TABLE 7.—ANALYSIS OF ORIGINAL WOOD AND WOOD AFTER 72 HOURS METHANOL EXTRACTION

| — | Lignin | Holo-cellulose | Cross and Bevan Cellulose | Xylan in Wood | Xylan in Holo-cellulose | Xylan in Cross and Bevan Cellulose |
|---|---|---|---|---|---|---|
| Original wood | 22·6 | 81·0 | 59·1 | 17·4 | 16·8 | 11·0 |
| Extracted wood (19·8 per cent. removed) .. | 10·6 | 63·0 | 55·0 | 16·4 | 11·7 | 8·4 |

All results expressed as percentages of original wood.

### 4. Properties of Lignin Isolated by Methanol Extraction

The isolated lignin was a buff-coloured powder which could be dissolved in methanol and re-precipitated by pouring into a large quantity of cold ether, when it came out as a flesh-coloured powder which rapidly darkened to brown in air. It was freely soluble in sodium hydroxide to give a brown solution, and it could be re-precipitated from this solution by acid. It was soluble in alcohol, chloroform, acetone, dioxan and hot cyclohexanol, but was very sparingly soluble in cold cyclohexanol. It was insoluble in benzene,

ether and petroleum ether. Ultramicroscopic examinations of the methanol and sodium hydroxide solutions showed that they were true and not colloidal solutions. These solubility properties distinguish it sharply from acid lignins such as Klason lignin.

The isolated lignin gave the typical pored-wood lignin colour reactions, namely, cherry red when treated with chlorine water followed by sodium sulphite, and colours with phenols and aromatic amines. With phloroglucinol it was a typical deep purple and with aniline a rich yellow. It gave no colour with ferric chloride.

By taking the temperature at which the lignin became sticky in the tube, fairly definite softening points could be obtained for the various samples of isolated lignin. Values varied between 110°C. and 132°C.

After heating for sixteen hours at 120°C. in sodium bisulphite solution containing 5 per cent. total sulphur dioxide, or in sulphite cooking liquor containing 6·1 per cent. total and 1·1 per cent. combined sulphur dioxide, the isolated methanol lignin was completely dissolved. Under the same conditions Klason lignin from the same wood was insoluble.

These properties of methanol lignin are therefore properties of the lignin in the wood which are not shared by acid lignins.

Repeated heating of the water-insoluble lignin in methanol at 150°C. resulted in its degradation to water-soluble materials. It appears therefore that the water-soluble material arose from breakdown of lignin during the extraction and that a percolation method would yield a less degraded lignin. The methanol extraction appears to be relatively free from the polymerization actions observed by Hewson and Hibbert (1943) since no methanol-insoluble residue was produced, as there was during methanol-HCl treatments of methanol lignin. Nevertheless prolonged methanol extraction did not completely delignify the wood. On boiling an aqueous solution of the water-soluble lignin with 3 per cent. sulphuric acid, a reddish-brown precipitate resembling Klason lignin was produced.

Methanol lignin, on treatment with dry hydrogen chloride in methanol, was changed to a black material soluble in sodium hydroxide but insoluble in the sodium bisulphite solution. Part of it was also precipitated as a black residue insoluble in methanol. Methylation with diazomethane gave a cream-coloured powder insoluble in sodium hydroxide.

These results are qualitatively the same as those obtained by Brauns with his spruce native lignin. However, the methoxyl content of methanol lignin from *E. regnans* (25-28 per cent.) was much higher than that of Brauns' native lignin (14·8 per cent.), and higher also than that of Klason lignin from *E. regnans* (22 per cent.).

Brauns and Brown (1938) concluded that sulphite solubility was dependent upon an easily methylated hydroxyl group. Since the isolated lignin was soluble in bisulphite it may be concluded that this group remained unmethylated.

Mackney (1940) showed that the methoxyl in holocellulose plus methoxyl in Klason lignin did not account for the total methoxyl in the wood of *E. regnans*. Increasingly drastic alkaline treatments of the wood caused loss of methoxyl from the holocellulose, but the unaccounted methoxyl remained constant. It appears therefore that this unaccounted methoxyl was originally attached to the lignin but was removed during the Klason treatment. The methoxyl in holocellulose was 1·2 per cent. and the unaccounted methoxyl 1·1 per cent., a total of 2·3 per cent. methoxyl not in Klason lignin. This is in agreement with the value of 2·37 per cent. methoxyl not in Klason lignin given in Table 4, and which is an entirely independent determination.

If it is assumed that all methoxyl not in holocellulose is associated with the native lignin, then we may calculate the expected methoxyl content of the native lignin of *E. regnans* from the data in Table 4 and Mackney's figure for the non-lignin methoxyl. The total methoxyl in the wood was 7·48 per cent. and therefore the methoxyl associated with the lignin was 6·28 per cent. The Klason lignin content of the wood was 22·6 per cent. Since methanol lignin yielded only 90 per cent. of Klason lignin, it must be assumed for purposes of calculation that this represents 24·9 per cent. of methanol lignin in the wood. The methoxyl content of the native lignin would therefore be $\frac{628}{24 \cdot 9} = 25 \cdot 2$ per cent. Similarly using Mackney's figure for methoxyl not in Klason lignin (2·3 per cent.) the methoxyl in Klason lignin would then be 5·18 per cent. of the wood, which contained 22·6 per cent. Klason lignin, and the expected methoxyl content of the Klason lignin is therefore $\frac{518}{22 \cdot 6} = 22 \cdot 9$ per cent.

It is recognized that these calculations are open to objections in that it is not known with any degree of certainty that the Klason lignin really does represent all the lignin and nothing but the lignin; furthermore, the calculations apply to the whole of the lignin in the wood, whereas only a third of it has been isolated as water-insoluble methanol lignin.

It is of interest to note that the syringyl compound 1-(4-hydroxy-3, 5-dimethoxyphenyl)-1, 2-propanedione isolated by Kulka *et al.* (1944) from hardwoods has a methoxyl content of 27·7 per cent., whereas the corresponding guaiacyl compound has a methoxyl content of 16·0 per cent.

## 5. Conclusions

Extraction of the wood of *Eucalyptus regnans* F.v.M. with methanol at 150°C. takes into solution a large part of the lignin in a form which retains the reactions of lignin in the wood. There is, therefore, some justification for referring to this lignin as native lignin.

## 6. Acknowledgments

This work was initiated by Dr. E. A. Hanson under the guidance of Dr. W. E. Cohen, and later carried on by other members of the staff of the Wood Chemistry Section of the Division of Forest Products. The authors wish to thank Mr. J. Sterling, Miss J. Meade, and Miss C. Emery of the Wood Chemistry Section for their assistance.

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# Mineral Chlorination Studies

## 3. The Chlorination of Australian Beryl

*By F. K. McTaggart, M.Sc.**

*Summary*

Optimum conditions for the decomposition by chlorine of beryl from Wodgina and Londonderry districts of Western Australia were determined and factors influencing the rate of reaction, such as fineness of grinding, catalysts, briquetting, and temperature, were investigated. Evidence was found for the presence of combined water in the beryls used. This was not eliminated at 1250°C. and prevented complete separation of the $AlCl_3$ and $BeCl_2$ produced when the latter was fractionally condensed in the range 200°–400°C. On resubliming the $BeCl_2$ and again condensing at 250°C. beryllium chloride free from aluminium was obtained. Other methods of separating the chlorides were investigated and it was found that among the organic solvents acetyl chloride is effective.

### 1. Introduction

During the last six or seven years the metal beryllium has assumed considerable importance both in the pure form and in the form of alloys of which beryllium–copper is perhaps the most widely used and best known. The demand for beryllium and its derivatives has increased steadily and although production has kept pace with requirements the processes in use for its production are not entirely satisfactory, as they involve some of the more difficult techniques known to industrial chemistry. Two main processes are in use, one depending on the electrolysis of the fused chloride and the other on the electrolysis of a fused complex fluoride. The former process may be carried out at relatively low temperatures (250°–800°C.) and low voltage (3–5 volts) but the beryllium is deposited in the form of flakes or powder and must be pressed and fused at 1300°C. under a suitable flux to yield ingots. The latter process yields the metal either in the form of an alloy or in the massive state but requires a working temperature of at least 1400°C. and a voltage of 70–80 volts. The present tendency overseas appears to favour the chloride electrolysis. Both processes involved, until recently, the breakdown of the ore by various means to yield intermediate compounds, for example, beryllium oxide, which was then chlorinated in the presence of carbon to yield anhydrous beryllium chloride.

Beryl, which is a silicate of beryllium and aluminium, is the only beryllium ore of general commercial importance. Notable deposits of beryl in pegmatite formations occur in certain parts of Australia, particularly in Western Australia at Wodgina, Londonderry, and elsewhere, and in the Boolcoomatta district of South Australia. These deposits have been worked to some extent but the beryl has been exported, and as yet no beryllium has been produced in this country. Because of the raw material potentially available it appears likely that Australia could satisfy a significant proportion of the present

* An officer of the Division of Industrial Chemistry.

demand for beryllium if the ore were processed locally. The above considerations form the background against which the present investigation was undertaken.

Winters and Yntema (1) have described a process for the production of anhydrous beryllium chloride by direct chlorination of beryl, the other chlorides formed, namely aluminium chloride and silicon tetrachloride, being separated by passing them through a tube held at 375°C. Under these conditions the beryllium chloride which has a b.p. of 520°C. is said to condense in the tube in a pure form, while the chlorides of aluminium, sub. pt. 178°C., and silicon, b.p. 57·6°C., pass through. The present paper describes the application of this process to beryls of Australian origin and the investigation of the various factors which influence the rate of chlorination. Some data are appended concerning other means of separation.

The theoretical formula for beryl, which is a beryllium aluminium silicate, may be expressed thus: $3BeO$, $Al_2O_3$, $6SiO_2$, i.e., 14 per cent. BeO, 19 per cent. $Al_2O_3$, and 67 per cent. $SiO_2$. In nature, however, these proportions are not adhered to strictly, the BeO varying from about 8 to 13 per cent. with corresponding variations in the percentages of the other constituents. Caesium, scandium, manganese, alkalis, and other elements may also be present in small quantities. The beryl crystal is one of the most complex silicates known, the Al, Be, and Si atoms being linked in a manner such as to bear no resemblance to oxide structure. As W. L. Bragg (2) says:—"The structure of beryl (aquamarine, emerald) may perhaps be considered as one of the most elegant of the many interesting coordinated structures displayed by silicates". Fig. 1 is a reproduction, taken from this book, of the structure of beryl:

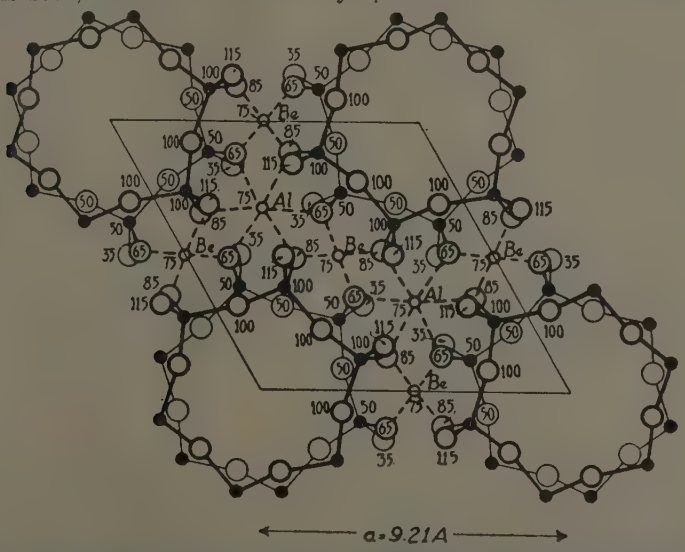



FIG. 1.—The structure of beryl, $Be_3Al_2Si_6O_{18}$. Note the $Si_6O_{18}$ rings. Superimposed oxygen atoms are symmetrically displaced. The reflection planes are at heights 0, 50, 100. (Reproduced from Bragg, 1937.)

The composition (see next section) of the beryl used by us was, however, sufficiently close to the theoretical for use to be made of the latter in calculating the proportions of beryl and carbon for briquetting and the approximate heat requirements of the reaction.

The reaction is essentially as follows:—

| | $3BeO$ | $+ Al_2O_3$ | $+ 6SiO_2$ | $+ 18C$ | $+ 18Cl_2$ | $\rightarrow 3BeCl_2$ | $+ 2AlCl_3$ | $+ 6SiCl_4$ | $+ 18CO$ |
|---|---|---|---|---|---|---|---|---|---|
| Mol. wts. .. | 25 | 102 | 60 | 12 | 71 | 80 | 133·5 | 170 | 28 |
| Mol. ratios by wt. | 75 | 102 | 360 | 216 | 1278 | 240 | 267 | 1020 | 504 |
| Wt. ratios .. | | 537 | | 216 | 1278 | | 1527 | | 504 |
| Heats of formation ($\triangle H$) in kilocals | 132? | 389·5 | 200 | | | 112·5 | 166·8 | 149 | 26·4 |
| Summation .. | 396 | 389·5 | 1200 | | | 337·5 | 333·6 | 894 | 475·2 |
| | 1985 K cals. | | | | | 2040 K cals. | | | |

There are insufficient data available at the present time for the calculation of the quantity of heat given out, or absorbed, per mole at the reaction temperature, or even of the free energies at room temperature, but from past experience with chlorinations of this nature and a consideration of the data given above, it would appear that the reaction is likely to be slightly exothermic at the reaction temperature and on a large scale it must be considered likely that sufficient heat would be generated to make external heating unnecessary provided the charge was initially at a sufficiently high temperature. This procedure has, for example, been found to be completely successful in the industrial scale chlorination of rutile. In any case, the heat requirements of the reaction would be small.

There are few references in the literature to the chlorination of beryl although many workers have prepared anhydrous beryllium chloride by chlorination of the oxide. In addition to those of Winters and Yntema (1) the only other chlorinations carried out on beryl appear to be (*a*) that referred to in a patent held by Portnov and Seferovich (3) and (*b*) one described by Fink (1). However, in none of these accounts are any details of proportions, reaction temperatures, reaction rates, etc., given. Fink stated that coarsely-ground beryl, without carbon, chlorinated readily at a red heat, but we were not able to confirm this. Portnov and Seferovich claimed that the reaction may be catalysed by small amounts of alkali metal chlorides.

## 2. Raw Materials

(i) *Beryl*

The beryls used in this investigation were of the massive variety. That from Londonderry was pale green in colour and was obtained from a large pegmatite formation worked for microcline felspar. That from the tantalite locality at Wodgina was white in color and of the variety known as rosterite containing about 1 per cent. of

caesium oxide. Londonderry beryl, of the type used in the work described here, has been described by Le Mesurier (5) and typical analyses given by him are as follows:—

Color: Milky white to pale green.

| | *1st. sample* | *2nd. sample* |
|---|---|---|
| | per cent. | per cent. |
| $SiO_2$ | 63·40 | 63·80 |
| $Al_2O_3$ | 21·28 | 17·26 |
| $Fe_2O_3$ | — | 0·80 |
| BeO | 9·56 | 12·58 |
| MgO | 0·16 | 0·02 |
| CaO | 0·20 | 0·30 |
| $Li_2O$ | 0·72 | 0·82 |
| $Na_2O$ | 1·24 | 1·38 |
| $K_2O$ | 0·16 | 0·20 |
| Ign. loss | 2·57 | 2·30 |
| | 99·29 | 99·46 |

The sample used contained 12·5 per cent. BeO and suffered the following losses on heating: to 120°C. 0·1 per cent., 120°–1000°C. 2·1 per cent., 1000°–1200°C. 0·2 per cent., making a total of 2·4 per cent. It was reserved mainly for the work on the separation of the chlorides because its composition approached more nearly that of the ideal beryl, 3BeO, $Al_2O_3$, $6SiO_2$, than the Wodgina ore. For this purpose it was crushed in a jaw crusher and ground in a roller mill to minus 10 mesh and finally ground in a porcelain ball mill to 98 per cent. minus 200 mesh.

Wodgina beryl has been described by Simpson (6) who gave the following analysis:—

| | |
|---|---|
| $SiO_2$ | 66·42 |
| $Al_2O_3$ | 17·97 |
| $Fe_2O_3$ | nil |
| BeO | 11·20 |
| FeO | nil |
| MnO | nil |
| MgO | nil |
| CaO | 0·30 |
| $Li_2O$ | 0·82 |
| $Na_2O$ | 1·01 |
| $K_2O$ | trace |
| $Cs_2O$ | 0·72 |
| Ign. loss | 2·20 |
| | 100·64 |

Other samples were reported to contain MnO. That used in this work contained 0·4 per cent. MnO and showed a loss on ignition to 120°C. 2·3 per cent., 120°–800°C. 1·1 per cent., 800–1000°C. 1·0 per cent., 1000°–1200°C. nil, making a total loss of 4·4 per cent.

This ore was used in the determination of reaction rates and for the experiments showing the influence of particle size. It was ground in a similar manner to the Londonderry ore but was finally screened and these fractions collected: — 100 + 150 mesh; — 150 + 200 mesh; — 200 + 270 mesh; and —300 mesh.

(ii) *Coal*

The coal used in these experiments was a black bituminous type and was crushed and ground until it had the following screen analysis: 10 per cent. retained on 50 mesh screen, 41·5 per cent. retained on 100 mesh screen, 29·5 per cent. retained on 150 mesh screen, 12·0 per cent. retained on 200 mesh screen, 6·0 per cent passed by 200 mesh screen.

The coal contained 11·5 per cent. ash made up of 7·6 per cent. $SiO_2$, 0·5 per cent. $Fe_2O_3$, 2·6 per cent. of other $R_2O_3$, and 0·8 per cent. undetermined alkalis, etc.

(iii) *Charcoal*

High-grade activated charcoal as used for decolorizing purposes was employed for most of the experiments on reaction rate. The ash content of this material was 8·0 per cent.

(iv) *Tar*

A light fraction of re-distilled vertical still tar which had the following physical and chemical characteristics *:

| | |
|---|---|
| Specific gravity | 1·06 |
| Free carbon | 5 per cent. by weight |
| Water | nil |

Distillation range:—

| | | |
|---|---|---|
| 0–170°C. | nil | |
| 170°–230°C. | 8·6 | per cent. (by volume) |
| 230°–300°C. | 28 | per cent. (by volume) |
| Total oils to 300°C. | 36·6 | per cent. (by volume) |
| Pitch content | 63 | per cent. (by weight) |

This tar, which was thin and dark brown in color, was found to be ideally suited for briquetting purposes.

## 3. Experimental

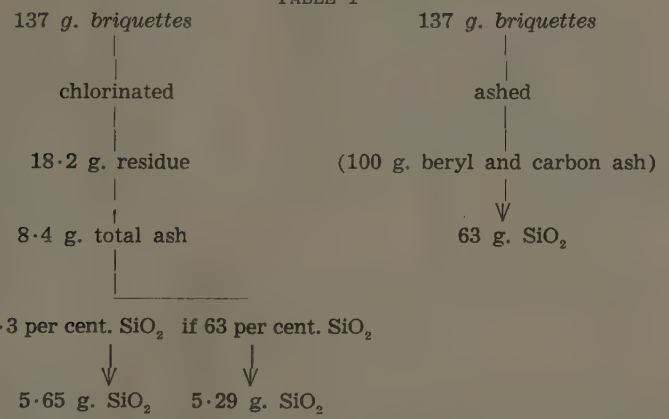
(i) *Briquetting*

The reaction between beryl (having the theoretical formula $3BeO.Al_2O_3.6SiO_2$), carbon, and chlorine has been shown above. From this it is seen that a briquetted mixture of beryl and carbon should contain 71 per cent. of beryl and 29 per cent. of carbon. However, this would only apply if the beryllium, aluminium, and silicon content of the mineral were attacked during chlorination to an equal degree. Initial experiments were made, using the above proportions, to determine whether equal attack did occur, and to this end a sample of briquettes

* We are indebted to Messrs. James Forbes (Tar Distillers), Melbourne, for this analysis, which is stated in the conventional tar manufacturers' way. This specification is very close to what is known in Australia as No. 1 vertical tar and could be described as "No. 1 vertical tar plus 3 per cent. of light oils".

containing by analysis 72·8 per cent. total ash (beryl plus carbon ash) and 27·2 per cent. carbon was ashed and an analysis for $SiO_2$ made on this ash. A figure of 63·0 per cent. $SiO_2$ was obtained. Briquettes from the same batch were then chlorinated until 91·6 per cent. conversion of the total ash content had been achieved. The residue which contained 54 per cent. carbon was ashed and the $SiO_2$ content was then found to be 67·3 per cent. To show that this difference is not significant when related to the actual quantities involved, Table 1 has been prepared.

TABLE 1




It shows the final discrepancy between the $SiO_2$ consumed theoretically (for uniform attack on the Al, Be, and Si content of the beryl) and that consumed actually, when 137 grams of briquettes were chlorinated. This discrepancy amounted to only 0·36 g. in 63 g. —less than 0·6 per cent. In other words the Al, Be, and Si in the beryl were, within close limits, attacked to an equal extent. Hence the theoretical proportions of beryl and carbon are correct, and the aim when making briquettes has always been to approximate closely the 71:29 ratio.

The method of briquetting has been fully described elsewhere (7), and was followed in this case both when using charcoal and coal. Too little carbon resulted in the briquettes crumbling badly during chlorination, while too much had no undesirable effect other than causing a waste of furnace space. The size of the briquette pieces used throughout the experimental work was minus ¼-in. mesh plus 1/32-in. mesh, in order to keep the conditions constant, but larger pieces up to ½-in. mesh or more were found to chlorinate satisfactorily, no diminution in reaction rate being noticeable.

The difference between briquettes made from coal and charcoal is shown later.

(ii) *The Laboratory Chlorination Furnace*

This is shown in Fig. 2. It consisted of a vertical silica tube furnace (A), wound with a heating element of 26-gauge platinum—20 per cent. rhodium wire, and fitted with a chlorine inlet tube (B),

thermocouple tube (C), and side outlet (D) for the gaseous reaction products. This side outlet was wound with a nichrome heating element to maintain it at a temperature slightly above 500°C. (E) was an opening used for filling the furnace, this opening being closed during chlorination by the ground plug (F).

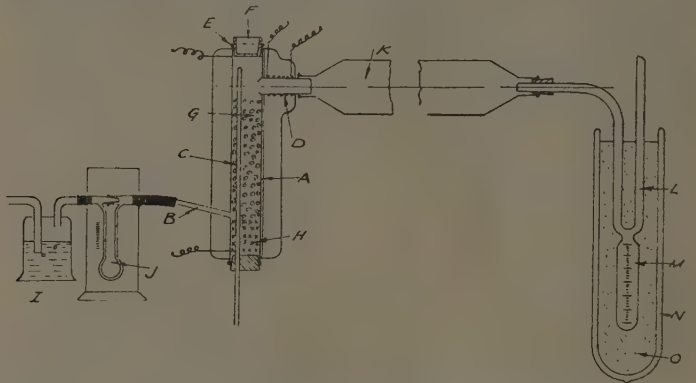



FIG. 2.—Laboratory chlorination furnace with apparatus for determination of reaction rates.

The charge (G) of briquetted beryl and carbon rested on a bed of silica chips (H), the latter ensuring that the whole of the charge was at a uniform temperature within the furnace. Chlorine was introduced into the furnace via the sulphuric acid bubbler (I) and the flowmeter (0–500 cubic centimetres per minute, orifice type) (J).

(iii) *Influence of Particle Size on Reaction Rate*

It has been shown that the aluminium, beryllium, and silicon in the beryl react during chlorination to an equal extent. Use was made of this fact in the determination of reaction rates. Owing to the difficulty of measuring the amounts of $BeCl_2$ and $AlCl_3$ produced during a given interval of time, these chlorides were condensed out completely and the $SiCl_4$ passed into a condenser. A measure of the volume of $SiCl_4$ collected in any given time, when other factors were constant (temperature, particle size, &c.) gave a measure of the reaction rate.

The apparatus used in addition to the chlorination furnace described above is shown on the right-hand side of Fig. 2. (K) is a pyrex glass tube 2 feet in length and 1½ in. in diameter. It was attached to the side outlet (D) of the furnace and served as an air condenser for the trapping of the $BeCl_2$ and $AlCl_3$. At room temperatures the $SiCl_4$ passed through this tube and was condensed in the U tube condenser (L), which was fitted with a receiving section (M) graduated in cc. The latter, with both arms of the condenser, was immersed in absolute alcohol cooled to — 25°C. by means of solid carbon dioxide, "dry ice." (N) was a vacuum flask containing the alcohol. A temperature above — 33·6°C., the boiling point of chlorine, was chosen to avoid condensation of the excess chlorine passing through the system.

Wodgina beryl screened as previously described to — 100 + 150, — 150 + 200, — 200 + 270, and minus 325 mesh was briquetted with B.D.H. decolourizing charcoal. The ash contents (beryl plus carbon ash) of these four batches of briquettes lay between the limits of 65 and 70 per cent. Charges of 100 g. — ¼-in + 1/32-in. mesh were used. The procedure was to place the charge in the furnace, close the top opening with the ground silica stopper, and attach the glass air condenser by means of a small amount of cement, consisting of equal parts of coarse asbestos fibre and alundum cement. The current was then turned on and the furnace and side outlet brought up to full working temperature. During this time a stream of dried nitrogen at 100-150 cc. per minute was passed through the furnace, and this was continued until all traces of moisture had been driven out of the system. The condenser for the $SiCl_4$ was then attached by means of a rubber stopper to the end of the air condenser and the vacuum flask containing the cooled alcohol placed in position. Chlorine was then passed into the furnace at a rate such that a slight excess appeared at the condenser outlet. This could be determined by analysis of the exit gases or more readily by calculation based on the amount of $SiCl_4$ condensing.

Table 2 shows the reaction rate, expressed as cc. of $SiCl_4$ evolved per fifteen minutes for the various sizes of beryl at temperatures of 800°, 1,000°, and 1,200°C.

TABLE 2

| Briquette | Beryl Mesh | Reaction Rate cc. of $SiCl_4$ per 15 mins. | | |
|---|---|---|---|---|
| | | Temp. 800° C | Temp. 1000° C | Temp. 1200° C |
| a .. .. | −100 +150 | 0·9 | 4·3? | 4·2 |
| b .. .. | −150 +200 | 2·5 | 4·3 | 4·8 |
| c .. .. | −200 +270 | 3·5 | 4·9 | 5·1 |
| d .. .. | −325 | 5·25 | 5·6 | 5·8 |

The influence of particle size is seen to be very marked at 800°C., but less so at 1000°C., and at 1200°C. It would appear necessary to grind the beryl at least to 90 per cent. minus 200 mesh. The reaction could then be carried out satisfactorily at 1000°C. Conversely, a temperature of 800°C. could be used with no great reduction in reaction rate, provided the beryl was ground to 100 per cent. minus 325 mesh. For large-scale work Table 2 allows a choice to be made and an optimum found between particle size and temperature.

(iv) *Influence of Temperature on Reaction Rate.*

In addition to the experimental work described above, reaction rates were determined at temperatures lower than 800°C., and the temperature at which reaction commenced was determined for each particle size. These results, together with those given in Table 2, are plotted in Fig. 3, the rate of reaction, given as volume in cc. of $SiCl_4$ per fifteen minutes, being plotted against temperature of reaction.

The shape of the curves is similar to that obtained for the reaction between rutile, carbon, and chlorine (7), and appears to be typical of heterogeneous reactions such as this. Reaction rate apparently depends on two factors:—

(*a*) The area of the solid surface which increases with degree of fineness, and the number of active surface spots which increases with temperature.

(*b*) The rate of diffusion of the chlorinating agent to, and the gaseous products away from, the solid surface which reaches a limiting value.

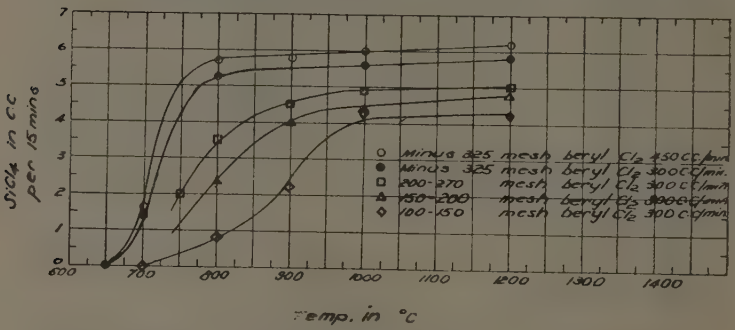

SiCl4 in cc per 15 mins
Temp. in °C
Minus 325 mesh beryl Cl2 450 cc/min.
Minus 325 mesh beryl Cl2 300 cc/min.
200-270 mesh beryl Cl2 300 cc/min.
150-200 mesh beryl Cl2 300 cc/min.
100-150 mesh beryl Cl2 300 cc/min.

FIG. 3.—Influence of temperature and particle size on reaction rate.

The use of a faster chlorine rate has the effect of promoting a more rapid removal of products from the active surface. This can be seen in the upper curve in Fig. 3, which was obtained when the chlorine rate was raised from 300 cc. per minute to 450 cc. per minute.

### (v) *Influence of Charcoal and Coal on Briquettes*

In sections (iii) and (iv) all briquetting was done with B.D.H. decolourizing charcoal. The cost of a material such as this would obviously be prohibitive in large-scale work, and it was therefore necessary to examine the effect of coal as the source of carbon in the briquettes. Hence, samples were made from Wodonga beryl of minus

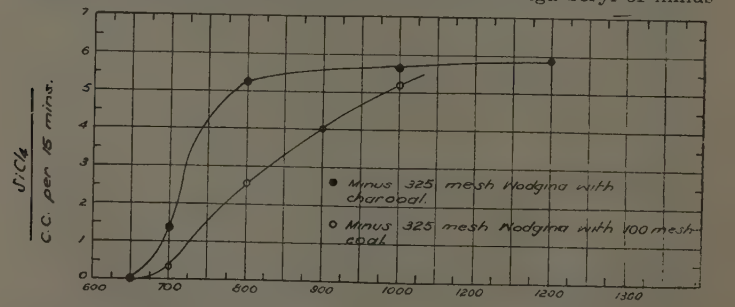



FIG. 4.—Reaction rates using coal and charcoal respectively.

325 mesh, 100 mesh coal, and tar, the briquetting being done in the standard manner. The porous masses produced were of a similar quality to the type previously used, had the same apparent porosity, and were of the same hardness. Reaction rates were determined at 1000°, 900°, 800°, and 700°C. The figures obtained are shown in graphical form in Fig. 4, together with a reproduction of the curve for Wodgina minus 325 mesh beryl plus charcoal.

There was little to choose between the coal and charcoal types at 1000°C., but at lower temperatures the former was unsatisfactory. It would appear that when using the coal-beryl briquettes a temperature of at least 900°C. is necessary for a reasonable reaction rate. Several batches of briquettes gave the same results.

(vi) *Effect of Addition of Alkali Metal Chloride on Reaction Rate and Difference between Wodgina and Londonderry Beryl*

Portnov and Seferovich (3) claimed that the reaction between beryl, carbon, and chlorine is catalysed by the addition of small, unstated quantities of alkali metal chlorides. Other workers have claimed similar results when chlorinating such minerals as rutile, ilmenite, and zircon. It was interesting, therefore, to apply the previously described technique for measuring reaction rates to this problem. At the outset it was realized that if these claims are correct the two types of beryl might be expected to show similar reaction rates since both have alkali contents of the same order. Therefore comparisons were first made between the two types. Both were ground to minus 325 mesh and briquetted with decolourizing charcoal and tar in the standard manner, the beryl-carbon ratio held within narrow limits. The variation of reaction rate with temperature for these samples is shown by curves (*a*) and (*c*) in Fig. 5.

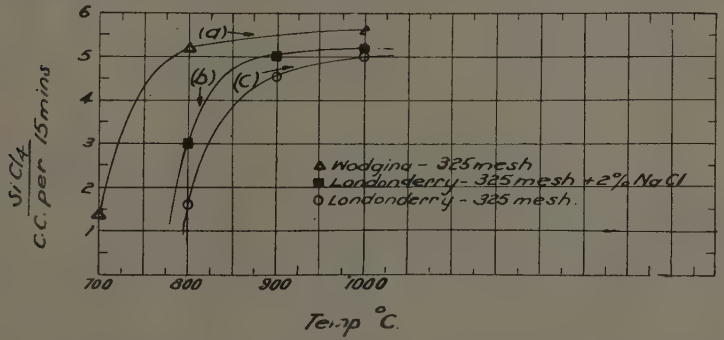



FIG. 5.—Reaction rates for different beryls and influence of alkali chloride.

It will be seen that there was a very marked difference between the two. The Wodgina beryl commenced to react at a temperature 100°C. below the Londonderry, and reacted faster at all temperatures up to 1000°C. No explanation can be given for this phenomenon, but it was evident that some other factor besides the alkali content was involved. The third curve shown (*b*) is for Londonderry beryl of minus 325 mesh plus 2 per cent. sodium chloride. To ensure good

mixing the beryl and salt were ground together in a ball mill to the above particle size, and then briquetted in the usual way. The curve shows a small but definite improvement over the same beryl without the addition of salt. A further sample of the beryl of the same size was mixed with sodium chloride in a jar without grinding, but on subsequent briquetting and chlorination reproduced curve (*c*). Hence the addition of an alkali chloride appeared to be effective in increasing the reaction rate, but this increase amounted to very little.

(vii) *Chlorine Efficiency*

The following typical chlorinations show that the chlorine efficiency was high. Under certain conditions it may be expected to approach 100 per cent.

TABLE 3

| Chlorination No. | Charge Data | | Temp. | Chlorine Rate | Time | Chlorine Used | Conversn. of Beryl | Residue Data | | Chlorine Efficiency |
|---|---|---|---|---|---|---|---|---|---|---|
| | Amt. | Compn. | | | | | | Amt. | Compn. | |
| | g. | | °C. | cc./min. | hr. | g. | % | g. | | % |
| 9 | 35 | 70 : 30 | 900 | 100 | 3¼ | 62 | 86 | 7 | 60 : 40 | 84 |
| 20 | 70 | „ | 980 | 100 | 5½ | 105 | 84 | 13 | „ | 90 |
| 33 | 70 | „ | 975 | 100 | 5¼ | 100 | 86 | 10 | „ | 98 |

Experience with the chlorination of rutile showed that better and more reliable results are to be obtained with large-scale chlorination than with laboratory experiments, and it appears certain that the same would apply in this case.

Winters and Yntema (1) and others have claimed that carbon tetrachloride is a better chlorinating agent than chlorine. We found no evidence to support this in the study of beryl.

(viii) *Attempted Separation of $AlCl_3$ and $BeCl_2$*

Winters and Yntema (1) chlorinated a briquetted mixture of beryl and carbon using chlorine or a mixture of chlorine and carbon tetrachloride. They stated that when they passed the mixed chloride vapours through a long pyrex glass tube held at 375°C. by means of an electrical heating element, pure $BeCl_2$ crystallized out in the tube while the other chlorides were not condensed, but passed through and were collected in further tubes or condensers at lower temperatures. $BeCl_2$ prepared in this way was stated to contain practically no $AlCl_3$, and only traces of silica and iron. Yntema stated (8) that their briquettes were heated to 800°C. prior to chlorinating at that temperature. Since this method of separation appeared very straightforward it was tried, according to the method described by these authors, but no separation such as was claimed was obtained.

The apparatus used is shown in Fig. 6.

The silica tube (P) 2 ft. 6 in. in length and 1¼ in. internal diameter was wound with the heating coil (Q), which served to heat (P) to any desired temperature (± 2½°C. throughout) up to 450°C.

(R) was a large bulb used to trap the chlorides not condensed in (P). If desired the condensing apparatus for $SiCl_4$ (see Fig. 2) could be attached to this bulb so that condensation of all the reaction products could be achieved.

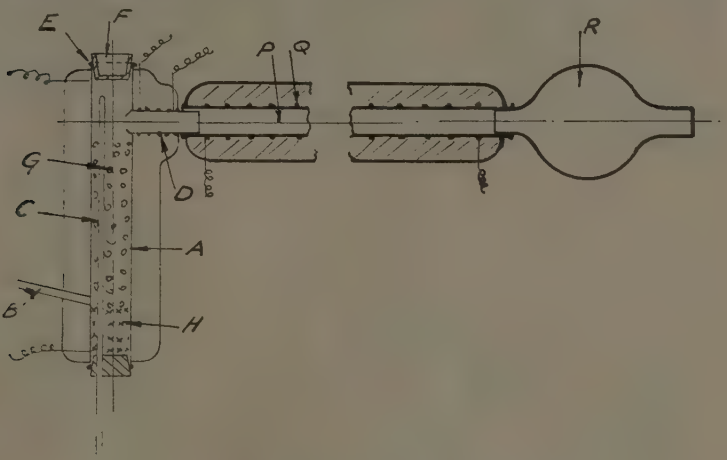



FIG. 6.—Apparatus for collection of chlorides.

During experimental chlorinations chlorine was passed into the furnace at 100 cc. per minute, so that the mixed chloride vapour was in tube (P) for 5-6 minutes and should, therefore, have had time to come to equilibrium temperature in (P). After each chlorination (P) was detached and the contents dissolved out with dilute hydrochloric acid, and the resulting solution analysed for beryllium and aluminium by the method of Kolthoff and Sandell (9), using 8-hydroxy-quinoline in the presence of ammonium acetate and acetic acid, to precipitate the aluminium and traces of iron.

Table 4 shows the results of four such chlorinations, during which the tube was maintained at 375°C.

TABLE 4

| Expt. No. | Temp. of Tube | Wt. of Chlorides in Tube | $AlCl_3$/$BeCl_2$ Ratio by Wt. | Furnace Data | | Conversn. | Chlorine Rate | Time |
|---|---|---|---|---|---|---|---|---|
| | | | | Charge | Residue | | | |
| | °C. | g. | | g. | | % | cc./min. | hr. |
| 21 | 375–385 | 2 | 1·3 : 1 | 70 | .. | .. | 75 | 5 |
| 27 | 370–380 | 3·5 | 1·7 : 1 | 100 | 68 | 32 | 50 | 6 |
| 36 | 375±2½ | 3·6 | 1·25 : 1 | 70 | 33 | 53 | 100 | 4 |
| 39 | „ | 3·5 | 2·5 : 1 | 70 | 27 | 62 | 100 | 5 |

Although not agreeing very well within themselves, probably because of the very small amount of chlorides collected, they show in each case an entirely different result from that claimed by Winters and Yntema.

That the vapours passed through the tube too quickly for temperature equilibrium to be established is disproved by No. 27, in which the chlorine rate was only 50 cc. per minute, and No. 21, in which it was 75 cc. per minute. No increased amount of chlorides was collected in these experiments over that collected in Nos. 36 and 39, so that the possibility of " sweeping out " of vapour by too rapid gas flow must be eliminated. In an attempt to achieve better separation a series of chlorinations was done with the collecting tube held at various temperatures between 200°C. and 400°C. The results are given in Table 5 and are graphed in Fig. 7.

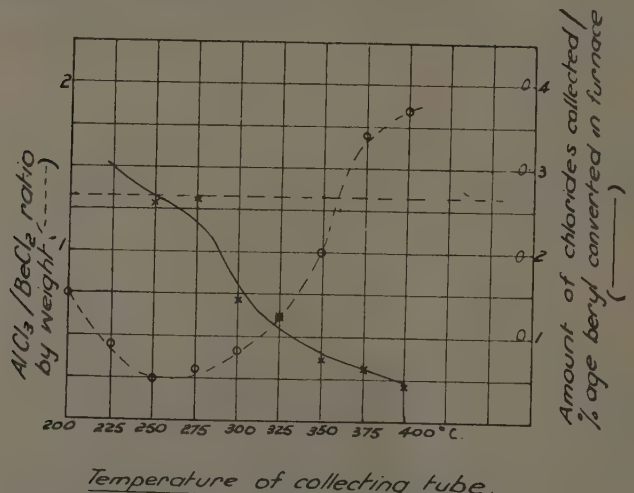



FIG. 7.—Influence of condenser temperature on selective deposition of $AlCl_3$ and $BeCl_2$.

It will be seen from Fig. 7 that there is a point of maximum enrichment of $BeCl_2$ at 250°C. The reason for this was not immediately evident, so further experiments were carried out for the purpose of elucidating the matter. Pure $Al_2O_3$ and BeO, both of which had been ignited to 1200°C., in the ratio of 17:10 by weight (corresponding approximately to the proportions of these oxides in beryl) were briquetted with charcoal in the standard manner and chlorinated at 900°-950°C. The $AlCl_3$ and $BeCl_2$ vapours formed were passed through the collecting tube which was held at 350°-360°C. It was found that pale yellow, almost white, crystals of $BeCl_2$ had formed in the tube and that the $AlCl_3$ had passed through. Thus the mixed oxides behaved very differently from the beryl. Two possible factors that might cause these anomalous results were recognized:—

(*a*) The presence of $SiCl_4$ vapour in the case of the beryl might be the cause of formation of loose compounds, thus changing the boiling point of chlorides.

(*b*) The presence of moisture during the chlorination in spite of the fact that the briquettes were heated to 800°C. prior to chlorination.

## TABLE 5

| Expt. No. | Temp. of Furnace | Temp. Data | | Charge | Residue Data | | Chlorine Rate | Time | Chlorides Collected in Tube | | | Total Chlorides Obt. | Remarks |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Tube | Tolerance | | Weight | Conversion | | | Weight | $AlCl_3/BeCl_2$ Ratio by Weight | Weight (g.)/ Percentage Beryl Converted | | |
| | °C. | °C. | °C. | g. | g. | % | cc./min. | hr. | g. | | | g. | |
| 45* | 1000 | 350 | ±5 | 100 | 40 | 75 | 100 | 5 | 9·2 | 1 | .. | .. | Briqs. not dried |
| 46* | 1000 | 300 | ,, | 100 | .. | .. | 100 | 5 | .. | 0·4 | .. | .. | ,, ,, ,, |
| 56* | 1100 | 300 | ,, | 100 | 25 | 80 | 200 | 4 | .. | 0·06 | .. | .. | Briqs. dried for 3 hr. at 1100° C. |
| 42 | 980 | 200 | ±2·5 | 70 | 7 | 92 | 100 | 5 | 11·7 | 0·74 | .. | 26 | Short collecting tube |
| 41 | 950 | 225 | ,, | 70 | 8 | 90 | 100 | 5 | 15·4 | 0·37 | .. | 32·4 | |
| 40 | 950 | 250 | ,, | 70 | 25 | 64 | 100 | 5 | 15·5 | 0·26 | 0·240 | .. | |
| 17 | 950 | 250 | ,, | 70 | 14 | 80 | 100 | 4 | 9 | 0·25 | .. | 21 | |
| 38 | 975 | 275 | ,, | 70 | 28 | 60 | 100 | 5 | 15·3 | 0·3 | 0·255 | .. | |
| 33 | 975 | 300 | ,, | 70 | 10 | 86 | 100 | 5 | 13·6 | 0·4 mean | 0·143 | 28·6 | |
| 18 | 975 | 300 | ,, | 70 | 13 | 81 | 100 | 4 | 10 | 0·38 | | 38? | |
| 34 | 975 | 325 | ,, | 70 | 10 | 86 | 100 | 5½ | 10·7 | 0·6 | 0·125 | 33·2 | |
| 35 | 980 | 350 | ,, | 70 | 16·5 | 78 | 100 | 5 | 7·3 | 1 mean | 0·075 | .. | |
| 25 | 980 | 350–360 | .. | 70 | 37 | 47 | 100 | 5 | 3 | 1·3 | .. | 18 | Temp. a little higher than 350° C. at times |
| 39 | 950 | 375 | ±2·5 | 70 | 27 | 62 | 100 | 5 | 3·5 | 2·5 mean | 0·060 | .. | Mean $AlCl_3/BeCl_2$ ratio (see Table 4 also) = 1·7 : 1 |
| 36 | 950 | 375 | ,, | 70 | 33 | 53 | 75 | 5 | 3·6 | 1·25 | | 13·6 | |
| 27 | 950 | 400 | ,, | 70 | 13 | 80 | 75 | 5 | 3·5 | 1·8 | 0·043 | 30? | Lower $Cl_2$ rate in attempt to get more chloride |

Mixed oxides (see text).

To investigate (*a*), a mixture of the oxides of aluminium, beryllium and silicon was made up, consisting of 19 per cent. $Al_2O_3$, 11 per cent. BeO, and 70 per cent. precipitated $SiO_2$—each of minus 300 mesh. This mixture was briquetted in the usual manner and chlorinated. Results are shown in Table 5. In Experiment No. 45 the collecting tube was held at 350°-360°C., while in No. 46 it was held at 290°-300C°. It will be seen that the figures for the $AlCl_3$ : $BeCl_2$ ratio agree closely with those obtained using beryl (e.g., Experiments 33 and 35). At first sight this appeared to confirm the view that the $SiCl_4$ was the disturbing factor, but it was considered desirable to investigate (*b*) thoroughly before coming to a definite conclusion.

The occurrence of a minimum point on the curve (Fig. 6), which indicated maximum enrichment of $BeCl_2$ at 250°C., may be explained by assuming that a practically constant fraction of the $AlCl_3$ produced in every chlorination was hydrolysed, and that this material collected in the tube, together with the anhydrous $BeCl_2$. There might also have been a small amount of $BeCl_2$ hydrolysed each time—but this would be less in amount than the $AlCl_3$, see below. Then at temperatures lower than 250°C. larger quantities of $AlCl_3$ would be obtained owing to condensation of unhydrolysed $AlCl_3$, which would have the effect of increasing the $AlCl_3$ : $BeCl_2$ ratio, while at temperatures higher than 250°C. smaller and smaller quantities of $BeCl_2$ would be retained; the hydrolysed $AlCl_3$ would still be present and the net effect again would be to increase the $AlCl_3$ : $BeCl_2$ ratio. That the $AlCl_3$ would be preferentially hydrolysed in this manner is in agreement with thermodynamical data for the two chlorides, and that the total $BeCl_2$ collected falls off gradually between 250°C. and 400°C. in agreement with the above reasoning is shown by the downward slope of the collection curve (also Fig. 6). At high temperatures practically nothing was collected in the tube, the material present being in the form of a brown sludge on the bottom of the tube. It appeared certain that this material was all in the hydrolysed form.

If this hydrolysis was taking place the moisture could come only from the charge because the chlorine was thoroughly dried through sulphuric acid and calcium chloride tubes, and furnace and collecting tubes were always dried for several hours at their respective running temperatures before chlorination was commenced. Firstly therefore, the mixed oxide briquettes described above were heated for several hours at 1100°C. and then chlorinated. The results (Experiment 56, Table 5) showed a marked improvement on previous chlorinations, the $AlCl_3$ : $BeCl_2$ being 0·06 : 1, compared to the previous best 0·25 : 1 As this demonstrated conclusively that moisture in the charge could cause lack of separation, attention was turned to beryl briquettes. In a series of experiments summarized in Table 6 beryl briquettes were dried at 1200°C. for 4–5 hours immediately prior to being chlorinated.

In Experiments Nos. 57, 59 and 60, briquettes were dried in the furnace itself in an atmosphere of nitrogen, and were then chlorinated at the same temperature—i.e., 1200°C. With the collecting tube at 370°C. little or nothing was retained while at 250°C. the ratio of $AlCl_3$ to $BeCl_2$ was 0·2 : 1, but analysis showed (column 14 and 15, Table 6) that some $AlCl_3$ was condensing. At 330°C. the ratio was 0·1 : 1 which was considered more satisfactory. However, when similar chlorinations were carried out at 1000°C.—a

## TABLE 6

| 1 | 2 | | 3 | 4 | 5 | 6 | 7 | | 8 | 9 | 10 | 11 | | 12 | | 13 | 14 | 15 | 16 | | 17 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Charge | | | | | | Residue | | | | | Chlorides in Tube | | | | | | | Glass Condenser | | |
| | | | | | | | | | | | | Loose Crystals | | Remainder | | | | | | | |
| Expt. No. | Wt. | Ash | History of Charge | Furnace Temp. | $Cl_2$ Rate—cc./min. | Time | Wt. | Ash | $SiCl_4$ Cond. | Reaction | Tube Temp. | Wt. | $AlCl_3$/$BeCl_2$ Wt. Ratio | Wt. | $AlCl_3$/$BeCl_2$ Wt. Ratio | Overall Ratio $AlCl_3$/$BeCl_2$ in Tube | Percentage Total $BeCl_2$ Produced Retained in Tube | Percentage Total $AlCl_3$ Produced Retained in Tube | Wt. of $A.C_2$ | Wt. of $BeCl_2$ | Remarks |
| | g. | % | | °C. | | hr. | g. | % | g. | % | °C. | g. | | g. | | | | | g. | g. | |
| 60 | 100 | 67 | Dried 4 hr. in furnace at 1200° C. | 1200 | 220 | $3\frac{3}{4}$ | 20 | .. | 81 | 82 | 250 | 8 | 0·035 | 13·1 | 0·37 | 0·2 | 80 | 15 | 17·2 | 4·6 | Temp. 250° too low |
| 59 | ,, | ,, | ,, | ,, | ,, | $4\frac{1}{2}$ | 22 | 80 | 78 | 79 | 330 | 5 | 0·04 | 6 | 0·17 | 0·1 | 55 | 5 | .. | .. | Optimum temp.? |
| 57 | ,, | ,, | ,, | ,, | 200 | $3\frac{1}{2}$ | .. | .. | 75 | 77 | 370 | Practically | | nil | collected | | .. | .. | 17·7 | 16·7 | Temp. 370° C. too high |
| 61 | ,, | ,, | ,, | 1000 | 150 | 4 | 38 | .. | 63 | 63 | 300 | 5 | 0·038 | 8·6 | 0·43 | 0·23 | 78 | 13·7 | 18·5 | 4·1 | |
| 75 | ,, | ,, | ,, | ,, | 100 | $4\frac{1}{2}$ | 39 | .. | 57 | 60 | 330 | 5 | 0·058 | 9·2 | 0·62 | 0·33 | 70 | 16 | 17·5 | 4·5 | |
| 77 | 96 | ,, | ,, | ,, | 150 | 5 | 26 | .. | 71 | 75 | 350 | 4 | 0·125 | 5 | 3·3 | 0·6 | 26 | 15 | 20·7 | 8·6 | Temp. 350° too high |
| 78 | ,, | 65 | Wodgina beryl dried at 800° C. | ,, | 100 | $4\frac{1}{2}$ | 24 | 75 | 63 | 65 | 330 | .. | .. | .. | .. | 0·8 | .. | .. | .. | .. | Cf. Expts. 34 and 35, Table 5 |
| 79 | 75 | ,, | Wodgina beryl dried 5 hr. at 1200° C. | ,, | 150 | 5 | 24 | 70 | 52 | 70 | ,, | .. | .. | .. | .. | 0·25 | 60 | 14 | 9·2 | 4·8 | Cf. 61 and 75 above |

temperature that must be regarded as a maximum for this type of reaction, owing to the rapid attack on silica, &c. by chlorine at high temperatures—results were disappointing. In Experiments 61 and 75 the charges were heated to 1200°C. for 4–5 hours in an electric muffle prior to chlorination, but the separation was little better than in previous cases cited in Table 5. Increasing the temperature of the collecting tube to 350°C. (Experiment 77) had the effect of reducing the amount of $BeCl_2$ retained, so that it appeared that 300°–330°C. was the optimum temperature for collection. Wodgina beryl briquettes treated and chlorinated under the same conditions (Experiment 79) gave almost identical results. It was found in these experiments that a quantity of the $BeCl_2$ was always condensed out in large, well-formed crystals on the upper part of the collecting tube and could be mechanically separated (see column 11, Table 6, Experiments 59, 61 and 75). These crystals seldom contained more than 4 per cent. of $AlCl_3$ but did not amount to more than 30–40 per cent. of the total $BeCl_2$ formed.

The use of baffles designed to bring about a more complete separation of these crystals was tried but was not successful. The bulk of the $AlCl_3$ in the tube was always in the brownish sludge on the bottom. It appeared to be partially hydrolysed and was a liquid above 250°C. No reason can be given at the present time for the increased separation found when chlorinating at 1200°C., but this temperature must be regarded as impracticable for general use.

The results obtained from all these experiments pointed clearly to the presence of moisture in the charge which, during chlorination, combined with part of the $AlCl_3$ to form a compound involatile up to 400°C. The question as to the source of this moisture remained unanswered. Kleeman (10) has shown that beryl from Boolcoomatta, South Australia, contains approximately 1·74 per cent. water given off between 120° and 800°C. He suggested that most of the water is given off at about 700°–800°C. but apparently did not confirm this. It appeared that four-hydroxyl groups replace one silicon-oxygen group in this type of beryl. We found that Londonderry beryl lost 1·95 per cent. water between 120° and 800°C., a further 0·15 per cent. between 800° and 1000°C., and suffered a further loss of weight of 0·2 per cent. between 1000° and 1200°C., which, on the evidence of the chlorination results, was still more water. Wodgina beryl lost 1·05 per cent. between 120° and 800°C., 1·05 per cent. between 800° and 1000°C., and practically nil between 1000° and 1200°C. Neither beryl can be heated above 1200°C. without sintering and fusing. The water remaining above 800°C. in either case would be sufficient to prevent complete separation as obtained by Winters and Yntema, and in view of our results it is a matter of doubt whether all the combined water is driven off even at 1200°C. Beryl from other sources may not contain hydroxy groups such as must be present in the types used by us, and with such " anhydrous " ores it should be possible to achieve separation readily. It must be concluded, however, that this is not possible with Londonderry or Wodgina beryl.

### 4. Resublimation of Mixed Chlorides

An attempt was made to effect a separation of the aluminium and beryllium chlorides by condensing them in a glass tube at room temperature and resubliming at temperatures of 360°–420°C. The

apparatus used is shown in Fig. 8. A 10-in. length of 2-in. diameter pyrex glass tubing (A) carrying a ground glass joint (B) was sealed to the side outlet of the chlorination furnace (C), and surrounded over a 6-in. length immediately adjacent to the furnace outlet, by a sliding heating element (D) the temperature of which was maintained at 430°C. The chlorides of aluminium and beryllium condensed in the region shown while the silicon tetrachloride passed through the tube and was condensed in the previously described condenser. Chlorination

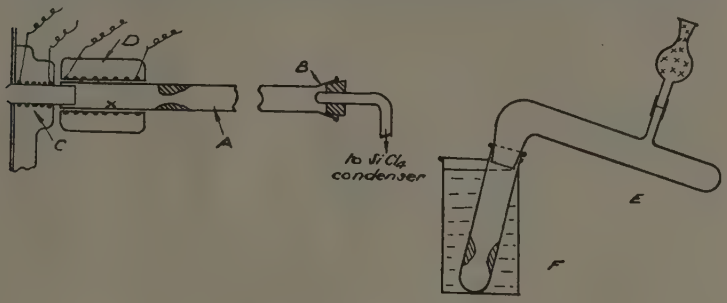



FIG. 8.—Differential sublimation apparatus.

of the charge was carried out in the usual manner with full precautions for drying, &c. At the conclusion of chlorination the whole system was swept out with nitrogen for ½ hour. The pyrex tube was then removed, quickly stoppered at each end with calcium chloride tubes, and sealed off at the position (X) in the blowpipe flame. A right-angled condenser tube (E) was fitted and the arm containing the chloride mixture was immersed in a salt bath (F) consisting of equal parts of sodium nitrate and sodium nitrite. The temperature of the bath was raised slowly to the desired value and left for ½ hour. The chlorides from each section were then dissolved out with dilute hydrochloric acid and analysed. The results are summarized in Table 7.

TABLE 7

| Expt. No. | Total Wt. of $AlCl_3$ and $BeCl_2$ Approx. | Temp. of Sublimation | Residual Chloride | | Sublimed Chloride | | Remarks |
|---|---|---|---|---|---|---|---|
| | | | Total | $BeCl_2/AlCl_3$ | Total | $BeCl_2/AlCl_3$ | |
| | g. | °C. | g. | | | | |
| 1 | 30 | 420 | 13·9 | 2·1 : 1 | 15·8 | 1 : 3·6 | $BeCl_2$ volatilized |
| 4 | 16 | 360 | 9 | 2·5 : 1 | 7 | 1 : 13 | |

It will be seen that the separation resulting from resublimation was in all cases very poor and again evidence was obtained for the presence of hydrolysed aluminium chloride. Thus in No. 1, Table 7, heating the mixture to 420°C. did not drive out a significantly greater quantity of this material than heating to 360°C. (No. 4). However, a quantity of beryllium chloride was lost at the higher temperature.

### 5. Resublimation of Beryllium Chloride

Since the beryllium chloride condensed in the range 225°–275°C. was contaminated with aluminium chloride in a form that appeared to be substantially involatile up to 400°C. it was anticipated that resublimation would yield a purer product. Furthermore, to avoid traces of $AlCl_3$ condensing with the resublimed $BeCl_2$ it seemed desirable to condense the latter again in a tube maintained at 250°C. Such experiments were carried out with success. Beryllium chloride containing 20 per cent. $AlCl_3$ was prepared in the manner and with the apparatus already described, with the condenser temperature at 250°C. (Fig. 6). When sufficient had been collected, the passage of chlorine was stopped, the glass bulb was removed from the end of the condenser and a second silica tube, similar to the first was attached. This was maintained at 250°C. and was fitted with a glass bulb at the end. The temperature of the first tube was then slowly raised to 420°C. during which a stream of nitrogen was passed through the system. On completion of the experiment the second tube was found to contain a mass of pure white, needle-like crystals of $BeCl_2$, in which no trace of aluminium could be detected using 8-hydroxy-quinoline reagent. In the first tube 2–3 grams of chlorides was usually obtained, these being in a semi-liquid or liquid form, and containing 40–60 per cent. $AlCl_3$. In the bulb at the end of the system was found a similar quantity of dry chlorides containing 60–70 per cent. $AlCl_3$.

The yield of $BeCl_2$ was approximately 40 per cent. based on the amount of beryl decomposed in the furnace. This rather low figure was probably due to the nature of the condensing tubes, a loss being sustained during each condensation; and it is probable that the use of a more efficient type of condenser would improve the yield. Data from two typical experiments are given below:—

TABLE 8

| No. | Beryl Consumed | After Resublimation | | | | | Yield $BeCl_2$ | First Bulb | |
|---|---|---|---|---|---|---|---|---|---|
| | | First Condenser | | Second Condenser | Second Bulb | | | Wt. | $\frac{AlCl_3}{BeCl_2}$ |
| | | Wt. | $\frac{AlCl_3}{BeCl_2}$ | $\frac{BeCl_2}{Wt.}$ | Wt. | $\frac{AlCl_3}{BeCl_2}$ | | | |
| | g. | g. | | g. | g. | | % | g. | |
| 3 | 40 | 2·2 | 0·8 | 5·0 | 3·0 | 2·0 | 42 | 19 | 3·75 |
| 4 | 45 | 2·0 | 1·2 | 5·4 | 3·2 | 2·0 | 39 | 20 | 4·0 |

### 6. Separation by Means of Solvents

Wurster (11) suggested the use of certain chlorides or oxychlorides of sulphur, carbon, phosphorus, and boron for the separation of the anhydrous chlorides of aluminium and beryllium. In each case the aluminium chloride was claimed to be readily soluble and the beryllium chloride practically insoluble. No figures were given for the solubilities. Compounds of practical interest that occur in this class include $SOCl_2$ b.pt. 78°C., $COCl_2$ b.pt. 8·2°C., and $POCl_3$ b.pt. 107°C. Attention was first turned to phosphorus oxychloride because it has

a lower volatility and is less poisonous than the others. The solubilities of the two chlorides were determined in this solvent at 25°C. and were found to be—

$AlCl_3$ 14·4 per cent., and $BeCl_2$ 20·6 per cent.,

a result which is in the opposite sense to that expected and which means that separation by this means is impracticable. Aluminium chloride readily forms an addition compound with phosphorus oxychloride especially if mixtures of the two are warmed. The whole mass may become solid and much larger quantities of the solvent than those given by Wurster were found to be necessary for complete solution of the aluminium chloride.

There is other evidence (Booth and Torrey, 12) that beryllium chloride is only slightly soluble in carbonyl chloride. However, the use of such a toxic compound must be regarded with disfavour for large scale work. It was thought that acetyl chloride, $CH_3COCl$ b.pt. 52°C., being a similar nature might prove a useful substitute, and the solubilities of the two chlorides in it were determined.

TABLE 9

| Temperature | Solubility | |
|---|---|---|
| | $BeCl_2$ | $AlCl_3$ |
| °C. | % | |
| 0 | 3·8 | "miscible" |
| 25 | 9·0 | " |

Aluminium chloride may be dissolved in acetyl chloride in any proportion, the solution gradually becoming more viscous. For example, 8 g. of anhydrous chloride in 15 g. cf acetyl chloride yields a syrup of the consistency of treacle. As the above figures appeared promising a series of experiments was carried out using mixtures of the chlorides made synthetically and from the chlorination of beryl. The results are summarized in Table 10.

TABLE 10

| Expt. No. | Approx. Wt. of $AlCl_3$ | Approx. Wt. of $BeCl_2$ | Volume of $CH_3COCl$ | Temp. | Recovered $BeCl_2$ | | | Remarks |
|---|---|---|---|---|---|---|---|---|
| | | | | | Wt. | $BeCl_2$ | $AlCl_3$ | |
| | g. | g. | cc. | °C. | g. | % | % | |
| 1 | 4 | 5 | 20 | 0 | 3·8 | 73 | 3·4 | Washed $BeCl_2$ on filtrate with 5 cc. $CH_3COCl$ at 0° C. |
| 2 | 4 | 5 | 20 | 0 | 3·5 | | | |
| 3 | 6·4 | 5·8 | 25 | 0 | 4·3 | 74 | 5 | |
| 4 | 8·1 | 7·4 | 30 | 0 | 4·8 | 65 | 1·3 | Washed with 10 cc. $CH_3COCl$ at 0° C. |
| 5 | 10 g. mixed from beryl chlorination | | 30 | 0 | 3 | .. | 4·5 | $BeCl_2$ not washed on filter |

It will be seen that a considerable degree of separation may be achieved by the use of acetyl chloride, which may be recoverd readily by distillation. Ferric chloride is readily soluble in acetyl chloride and is therefore removed with the aluminium.

## 7. Conclusion

An attempt was made to separate the chlorides of aluminium and beryllium by fractional condensation following direct chlorination of two beryls of Australian origin. It is believed that the presence of (OH) groups in the crystal lattice of the beryls was responsible for the failure to effect separation. Attempts to separate the aluminium chloride from the beryllium chloride by first collecting both chlorides and then subliming off the former by careful control of temperature were not successful. However, beryllium chloride collected at 250°C. and containing 10–20 per cent. aluminium chloride was obtained free from aluminium by resubliming and again condensing the beryllium chloride in a tube maintained at 250°C.

Acetyl chloride was found to be effective in separating the two chlorides but phosphorus oxychloride was not suitable. The solubilities of aluminium and beryllium chlorides in phosphorus oxychloride and acetyl chloride were determined.

## 8. Acknowledgments

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# Studies in Cement-Aggregate Reaction

## VII.—The Effect of Storage Conditions on Expansion and Tensile Strength Changes of Mortar

*By H. E. Vivian, B.Sc.Agr.**

*Summary*

Mortars containing high-alkali cement and reactive aggregate were stored under various conditions. Although expansion was affected by the environment (negatively in dry air; positively in other conditions), cracks were produced and significant reductions in tensile strength occurred in all mortars.

### 1. Introduction

It was shown by Stanton† (1940) that small mortar test pieces containing reactive aggregate and high-alkali cement expanded abnormally in a moist but not in a dry atmosphere. This suggests that different storage conditions, by affecting the amount of uncombined water in mortar, modify the expansion of reacted aggregate particles. Although similar mortars stored in water did not expand abnormally, more recent work by Stanton** (1943) has shown that storage in 1 and 2 per cent. sodium hydroxide solutions caused significant expansions. An attempt is made in this paper to show how storage conditions affect the expansion and the tensile strength of mortar.

### 2. Materials

TABLE 1.—CHEMICAL COMPOSITION OF CEMENT

| *Oxide* | *Percentage* |
|---|---|
| $SiO_2$ .. .. .. .. .. | 22·14 |
| $Fe_2O_3$ .. .. .. .. | 2·38 |
| $Al_2O_3$ .. .. .. .. | 4·94 |
| CaO .. .. .. .. .. | 64·12 |
| MgO .. .. .. .. .. | 1·08 |
| $SO_3$ .. .. .. .. .. | 1·84 |
| $Na_2O$ .. .. .. .. | 0·45 |
| $K_2O$ .. .. .. .. .. | 0·81 |
| Loss on ignition .. .. .. | 1·88 |

The reactive aggregate was a mixture consisting of five parts by weight of the reactive component plus 95 parts of the non-reactive component. The reactive component was an opaline rock (V.17) from Butcher's Ridge, East Gippsland, Victoria, crushed and sieved to − 18 + 52 B.S.S. mesh, and the non-reactive component was a quartz sand from either Leighton Buzzard, England, or Paringa, South Australia. These non-reactive sands were used in control mortars. Unless otherwise specified Leighton Buzzard sand was the non-reactive component used. The water : cement : aggregate ratio of all mortars was 0·5 : 1 : 2 by weight at the time of mixing.

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* An officer of the Division of Industrial Chemistry.

† Stanton, T. E. (1940).—*Proc. Amer. Soc. Civ. Engrs.* 66: 1781.

** Stanton, T. E. (1943).—*Proc. Amer. Soc. Test. Mater.* 43: 875.

## 3. Experimental

(i) *Mortar Bar Expansions*

Mortar bars, made from cement and reactive aggregate, were stored at room temperature under the following conditions: (*a*) in dry air*, (*b*) in moist air, (*c*) in 1 per cent. sodium hydroxide solution, and (*d*) in water.

After storage for 41 days some test bars from each were changed over to each of the other three storage conditions, and kept in these for the remainder of the test period. In this way the effects of pairs of storage conditions were observed. Some test bars were kept for the full test period in their initial environments. Mortar blocks of similar composition, stored under the same conditions as the test bars, were broken periodically and examined by means of a binocular microscope at 30 diameters magnification.

The expansions of these bars stored under different conditions are shown in Table 2. During the first 41 days storage the water vapour pressure in dry air storage may have exceeded 1 mm. Hg, since the partially spent calcium chloride was not replaced by the fresh desiccant frequently enough. As the results are not of exact quantitative significance this is unimportant.

Conclusions from mortar expansions are:—

1. Mortars did not expand significantly when stored in dry air. When stored in water they expanded very slowly but when stored in moist air or 1 per cent. sodium hydroxide solution they expanded rapidly.

2. Unexpanded motars taken from dry air and placed either in moist air, 1 per cent. sodium hydroxide solution, or in water, expanded very rapidly for a short time, after which their expansion rates decreased. These initial expansion rates were so high that it seemed probable that opal had undergone considerable attack by alkalis during storage in dry air and that when water was made available it was absorbed rapidly.

3. Expanded test bars, stored initially in moist air, expanded rapidly for a short time on being changed to water or 1 per cent. sodium hydroxide solution, after which their expansion rates decreased. This is similar to the previous result (2) and indicates that the reaction product can absorb large amounts of water in a short time.

4. Mortar which had expanded in 1 per cent. sodium hydroxide solution contracted slightly when changed to moist air but later expanded rapidly. When changed to water similar bars continued expanding very slowly. This suggests that the alkali (or sodium hydroxide) content of the surrounding solution affects the expansion rate of mortar.

5. Bars initially stored in water expanded excessively when changed to 1 per cent. sodium hydroxide solution. This suggests that either the increased concentration of alkalis in the storage solution

* Dry air is a term used here in contrast with moist air. It refers to storage in an atmosphere above calcium chloride ($CaCl_2 - CaCl_2.H_2O$) and having a water vapour pressure less than 1 mm. Hg at 25°C.

## Table 2.—Percentage Expansions of Test Bars

| Time after Fabrication (Days) | Dry Air | | | | Moist Air | | | | 1 per cent. Sodium Hydroxide Solution | | | | Water. | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 1 | 2 | 3 | 4 | 1 | 2 | 3 | 4 | 1 | 2 | 3 | 4 |
| 7 | −0·019 | −0·013 | −0·014 | −0·014 | +0·005 | +0·013 | +0·007 | ±0·000 | +0·011 | +0·019 | +0·009 | +0·017 | +0·017 | +0·023 | +0·013 | +0·012 |
| 12 | −0·037 | −0·027 | −0·018 | −0·026 | 0·007 | 0·020 | 0·027 | +0·015 | 0·032 | 0·055 | 0·047 | 0·051 | 0·017 | 0·027 | 0·016 | 0·014 |
| 18 | −0·042 | −0·027 | −0·020 | −0·030 | 0·165 | 0·177 | 0·189 | 0·150 | 0·144 | 0·188 | 0·177 | 0·186 | 0·024 | 0·029 | 0·020 | 0·023 |
| 27 | −0·029 | +0·031 | +0·035 | −0·018 | 0·497 | 0·498 | 0·521 | 0·438 | 0·301 | 0·349 | 0·344 | 0·348 | 0·067 | 0·042 | 0·046 | 0·058 |
| 34 | −0·015 | 0·051 | 0·064 | −0·017 | 0·631 | 0·658 | 0·673 | 0·592 | 0·375 | 0·437 | 0·431 | 0·424 | 0·088 | 0·053 | 0·060 | 0·072 |
| 41* | −0·004 | 0·061 | 0·067 | −0·005 | 0·743 | 0·769 | 0·784 | 0·692 | 0·446 | 0·502 | 0·500 | 0·501 | 0·099 | 0·061 | 0·065 | 0·086 |
| Changed to— | Dry Air | Moist Air | 1 per cent. Sodium Hydroxide Soln. | Water | Dry Air | Moist Air | 1 per cent. Sodium Hydroxide Soln. | Water | Dry Air | Moist Air | 1 per cent. Sodium Hydroxide Soln. | Water | Dry Air | Moist Air | 1 per cent. Sodium Hydroxide Soln. | Water |
| 46 | +0·012 | +0·225 | +0·182 | +0·097 | +0·773 | +0·859 | +0·994 | +0·906 | +0·417 | +0·491 | +0·555 | +0·517 | +0·063 | +0·051 | +0·075 | +0·090 |
| 48 | 0·002 | 0·260 | 0·179 | 0·099 | 0·760 | 0·851 | 0·993 | 0·904 | 0·404 | 0·489 | 0·565 | 0·517 | 0·049 | 0·049 | 0·073 | 0·090 |
| 50 | −0·004 | 0·286 | 0·186 | 0·099 | 0·751 | 0·855 | 0·992 | 0·903 | 0·399 | 0·482 | 0·582 | 0·516 | 0·047 | 0·044 | 0·074 | 0·090 |
| 55 | −0·011 | 0·387 | 0·242 | 0·115 | 0·736 | 0·852 | 0·996 | 0·907 | 0·387 | 0·485 | 0·622 | 0·539 | 0·035 | 0·045 | 0·085 | 0·095 |
| 63 | −0·027 | 0·511 | 0·293 | 0·122 | 0·714 | 0·862 | 0·994 | 0·902 | 0·365 | 0·546 | 0·679 | 0·556 | 0·020 | 0·042 | 0·118 | 0·094 |
| 70 | −0·033 | 0·570 | 0·350 | 0·136 | 0·707 | 0·863 | 1·000 | 0·906 | 0·355 | 0·715 | 0·732 | 0·562 | 0·010 | 0·044 | 0·152 | 0·102 |
| 84 | −0·044 | 0·709 | 0·409 | 0·142 | 0·682 | 0·924 | 0·999 | 0·906 | 0·332 | 0·965 | 0·797 | 0·579 | −0·006 | 0·039 | 0·289 | 0·101 |
| 98 | −0·050 | 0·761 | 0·473 | 0·146 | 0·669 | 0·983 | 1·005 | 0·908 | 0·320 | 1·117 | 0·888 | 0·603 | −0·018 | 0·047 | 0·486 | 0·107 |
| 112 | −0·062 | 0·809 | 0·521 | 0·148 | 0·659 | 1·046 | 1·007 | 0·910 | 0·308 | 1·173 | 0·950 | 0·600 | −0·039 | 0·047 | 0·671 | 0·107 |
| 140 | −0·064 | 0·878 | 0·592 | 0·147 | 0·649 | 1·198 | 1·009 | 0·910 | 0·295 | 1·322 | 1·046 | 0·605 | −0·054 | 0·057 | 0·980 | 0·108 |
| 196 | −0·071 | 0·988 | 0·667 | 0·155 | 0·641 | 1·362 | 1·025 | 0·914 | 0·285 | 1·469 | 1·156 | 0·603 | −0·057 | 0·078 | 1·370 | 0·110 |
| 252 | −0·072 | 1·023 | 0·701 | 0·154 | 0·645 | 1·409 | 1·048 | 0·917 | 0·289 | 1·583 | 1·225 | 0·606 | −0·055 | 0·093 | 1·576 | 0·111 |
| 308 | −0·113 | 1·206 | 0·712 | 0·167 | 0·644 | 1·538 | 1·091 | 0·917 | 0·288 | 1·692 | 1·255 | 0·603 | −0·059 | 0·122 | 1·703 | 0·113 |
| 364 | −0·116 | 1·205 | 0·743 | 0·157 | 0·640 | 1·546 | 1·124 | 0·918 | 0·284 | 1·692 | 1·287 | 0·606 | −0·056 | 0·122 | 1·854 | 0·116 |

* Test bars changed to different storage conditions 41 days after fabrication.

prevents the continued diffusion of alkalis out of the mortar or, more probably, that the opal is being attacked by sodium hydroxide which diffuses from the storage solution into the mortar. When similar mortars were changed from water to moist air they contracted slightly and then, after a period of comparative stability, expanded slowly. This is probably due to the mortar containing little alkali and much uncombined water.

6. Mortar bars stored initially either in moist air, in 1 per cent. sodium hydroxide solution or in water, showed reduced expansion rates when changed to dry air. Their eventual contractions indicate that the availability of uncombined water affects the expansion of reacting opal or the reaction product.

Observations on these mortars are summarized (*a*) after the first 41 days storage in each environment, and (*b*) after subsequent storage.

(*a*) *Storage for first* 41 *days*

(1) *In dry air.*—A few small spots developed on the surface of the mortar. When freshly broken the cement appeared dry. Opal particles were slightly softened but not wet. Numerous short very fine cracks in the mortar were associated with opal particles.

(2) *In moist air.*—Numerous wet spots developed on the mortar surfaces. Cement in freshly broken mortar appeared slightly moist. Changes observed in opal particles during reaction were: (*a*) softening, (*b*) a tendency to form a jelly-like product, (*c*) some were finally converted to viscous liquid. The numerous cracks through the mortar were always associated with reacting opal particles and were filled only for part of their length with the reaction product.

(3) *In sodium hydroxide solution* (1 *per cent.*).—The mortar surfaces were coated thickly with gelatinous material. In freshly broken specimens the cement appeared very wet especially near original external surfaces. Opal particles throughout the mortar had been attacked and in many cases had been converted to viscous liquid. The mortar was cracked extensively and the cracks were completely filled with reaction product.

(4) *In water.*—Only a few spots of white gelatinous material developed on the surfaces of the mortar. Cement in freshly broken specimens appeared very wet. Opal particles had reacted and softened and in some cases had been converted to viscous liquid. The mortar was traversed by numerous fine cracks which were associated with reacted particles. The cracks were completely filled with the reaction product.

(*b*) *Storage from* 41 *days to* 364 *days*

(1) Mortars changed from dry air to moist air, to 1 per cent. sodium hydroxide solution, and to water, cracked extensively and their reactive particles underwent considerable change. In moist air storage the reaction product appeared to remain in the gel state and did not fill the cracks completely. In 1 per cent. sodium hydroxide solution and in water storage the cracks were completely filled with reaction product which appeared to have been converted to viscous liquid.

(2) All mortars, when changed to dry air, dried out slowly. The reaction product in cracks and in spaces occupied originally by opal particles, appeared to shrink considerably.

(3) Cracks in mortars changed from moist air to 1 per cent. sodium hydroxide solution or to water became completely filled with reaction product.

(4) Mortars changed from water to 1 per cent. sodium hydroxide solution and *vice versa* showed very little change. The reactive particles in mortars originally stored in water appeared to be more completely attacked and softer after storage in 1 per cent. sodium hydroxide solution.

(5) Mortars originally stored in 1 per cent. sodium hydroxide solution or in water showed no change after storage in moist air.

(6) All mortars retained in their original environments showed no apparent changes.

(ii) *Losses from Mortars by Heating at* 110°*C.*

Some mortar blocks were made with non-reactive aggregate and some with reactive aggregate. These mortars, stored under the various conditions for periods up to 114 days, were heated in an electric oven for one hour at 110°C.

TABLE 3.—THE PERCENTAGE LOSSES FROM MORTARS AT 110°C

| Aggregate | Time after Fabrication (Days) | Dry Air | Moist Air | Sodium Hydroxide Soln. (1 per cent.) | Water |
|---|---|---|---|---|---|
| Non-reactive .. | 1 | 11·0 | 11·0 | 10·7 | 10·8 |
| | 8 | 5·9 | 8·6 | 9·5 | 9·3 |
| | 21 | 4·0 | 8·0 | 9·5 | 9·4 |
| | 42 | 3·1 | 8·0 | 9·2 | 9·1 |
| | 77 | 2·1 | 7·5 | 8·9 | 9·0 |
| | 114 | 1·5 | 7·5 | 8·6 | 8·8 |
| Reactive .. | 1 | 11·0 | 11·6 | 11·3 | 11·4 |
| | 8 | 6·6 | 8·2 | 9·7 | 9·5 |
| | 21 | 4·1 | 8·2 | 10·3 | 9·3 |
| | 42 | 3·4 | 8·3 | 10·7 | 9·6 |
| | 77 | 2·4 | 8·0 | 10·7 | 8·9 |
| | 114 | 1·8 | 8·2 | 10·8 | 9·4 |

The results, which are shown in Table 3, indicate the relative amounts of uncombined water in each mortar. It is recognized that these losses are of only qualitative significance since some combined hydrate water is lost at this temperature and carbon dioxide is absorbed by the cement during heating. As all the losses at any given time should have an approximately constant error, the following conclusions concerning the amounts of uncombined water in mortar stored under the various conditions seem reasonable:—

(1) The amount of uncombined water in mortar stored in dry air was much lower than that in mortar stored under other conditions.

(2) The amount of uncombined water in mortar stored in moist air was lower than that in mortar stored either in 1 per cent. sodium hydroxide solution or in water. The differences were comparatively small.

(3) The somewhat high losses from reactive aggregate mortar when stored in 1 per cent. sodium hydroxide solution were probably due to the large quantity of water in the reaction product.

(iii) *The Behaviour of Alkalis in Mortar Stored in Water and 1 per cent. Sodium Hydroxide Solution*

Blocks of mortar, each weighing approximately 110 g., and of similar composition to those used in the experiments previously described, were stored in 250 ml. of each medium at room temperature. Some results indicating the behaviour of alkalis are shown in Table 4.

TABLE 4.—THE AMOUNTS OF SODIUM AND POTASSIUM HYDROXIDES FOUND IN SOLUTIONS IN WHICH MORTARS WERE STORED

| Pre-treatment | Time in Storage Solutions (Days) | In Water | | In 1 per cent. Sodium Hydroxide Solution | |
|---|---|---|---|---|---|
| | | Non-reactive Aggregate | Reactive Aggregate | Non-reactive Aggregate | Reactive Aggregate |
| | NaOH (g./100 ml.) | | | | |
| Mortars placed in storage solutions 20 hours after fabrication | Nil | 0·0025 | 0·0025 | 1·0275 | 1·0275 |
| | 7 | 0·0520 | 0·0471 | 0·9724 | 0·8976 |
| | 14 | 0·0612 | 0·0546 | 1·0022 | 1·0026 |
| | 28 | 0·0788 | 0·0693 | 1·0275 | 1·0553 |
| | KOH (g./100 ml.) | | | | |
| | Nil | Trace | Trace | Trace | Trace |
| | 28 | 0·1424 | 0·0740 | 0·0360 | 0·0500 |
| | NaOH (g./100 ml.) | | | | |
| Mortars placed in storage solutions after 28 days storage in moist air | 7 | 0·0320 | 0·0304 | .. | .. |
| | KOH (g./100 ml.) | | | | |
| | 7 | 0·0466 | 0·0325 | .. | .. |

Conclusions are:—

(1) Alkalis were lost from all mortars which were stored in water. Mortars which contained reactive aggregate lost slightly less alkalis than those which contained non-reactive aggregate.

(2) After 28 days storage in water most of the alkalis were lost from the non-reactive aggregate mortar. During the same period most of the sodium hydroxide and about half of the potassium hydroxide were lost from the reactive aggregate mortar.

(3) Mortar stored in 1 per cent. sodium hydroxide solution at first appeared to take up sodium hydroxide from the storage solution, but later seemed to lose it again. The latter effect is probably due to some of the gel being extruded from the mortar and dispersed in the storage solution as small amounts of silica have been detected in it.

(4) The rate at which potassium hydroxide was lost from mortar was decreased by storing in 1 per cent. sodium hydroxide solution.

(iv) *Tensile Strength Changes of Mortars Stored under Various Conditions*

With the exception of the non-reactive rounded quartz sand from Paringa, South Australia, which was substituted for Leighton Buzzard sand, the materials and mixtures were the same as those used in sections (i), (ii) and (iii). Test bars and briquettes were stored under each of the following conditions: (*a*) in dry air; (*b*) in moist air; (*c*) in 1 per cent. sodium hydroxide solution; and (*d*) in water.

The relations between expansion and tensile strength of mortars at various ages stored under different conditions are shown in Table 5. Each recorded tensile strength, which is the mean of three determinations, is given to the nearest 10 lb. per sq. in. Differences between the maximum and minimum values within each group of three were generally lower for mortars containing reactive aggregate (less than 60 lb. per sq. in.) than for those containing non-reactive aggregate (50-110 lb. per sq. in.). Chance differences in the test pieces and testing procedure seem to cause these variations.

TABLE 5.—THE RELATIONS AT VARIOUS AGES BETWEEN EXPANSION AND TENSILE STRENGTH OF MORTARS CONTAINING NON-REACTIVE AND REACTIVE AGGREGATES WHEN STORED UNDER DIFFERENT CONDITIONS

| Storage | Time after Fabrication | Non-reactive Aggregate | | Reactive Aggregate | |
|---|---|---|---|---|---|
| | | Expansion | Tensile Strength | Expansion | Tensile Strength |
| | days | % | lb./sq. in. | % | lb./sq. in. |
| In dry air .. .. | 1 | ±0·000 | 120 | ±0·000 | 160 |
| | 6 | −0·018 | 370 | −0·016 | 370 |
| | 15 | −0·041 | 530 | −0·029 | 330 |
| | 22 | −0·059 | 510 | −0·040 | 330 |
| | 29 | −0·073 | 470 | −0·052 | 320 |
| | 36 | −0·083 | 480 | −0·065 | 330 |
| | 43 | −0·090 | 510 | −0·069 | 270 |
| | 57 | −0·102 | 550 | −0·081 | 290 |
| | 85 | −0·121 | 600 | −0·092 | 220 |
| | 113 | −0·137 | 560 | −0·108 | 230 |
| | 141 | −0·163 | 530 | −0·137 | 380 |
| | 169 | −0·187 | 600 | −0·155 | 260 |
| | 197 | −0·194 | 590 | −0·164 | 270 |
| In moist air .. | 1 | ±0·000 | 100 | ±0·000 | 170 |
| | 6 | −0·007 | 360 | +0·004 | 350 |
| | 11 | −0·006 | 370 | 0·015 | 340 |
| | 16 | −0·003 | 440 | 0·057 | 210 |
| | 23 | −0·004 | 470 | 0·183 | 140 |
| | 30 | −0·008 | 450 | 0·310 | 130 |
| | 44 | −0·007 | 410 | 0·617 | 100 |
| | 58 | −0·004 | 360 | 0·837 | 80 |
| | 86 | −0·007 | 330 | 1·059 | 60 |
| | 114 | −0·007 | 350 | 1·244 | 40 |
| | 142 | −0·017 | 370 | 1·351 | 70 |
| | 170 | −0·014 | 440 | 1·383 | 70 |
| | 198 | −0·015 | 410 | .. | .. |

TABLE 5.—THE RELATIONS AT VARIOUS AGES BETWEEN EXPANSION AND TENSILE STRENGTH OF MORTARS CONTAINING NON-REACTIVE AND REACTIVE AGGREGATES WHEN STORED UNDER DIFFERENT CONDITIONS —*continued.*

| Storage | Time after Fabrication | Non-reactive Aggregate | | Reactive Aggregate | |
|---|---|---|---|---|---|
| | | Expansion | Tensile Strength | Expansion | Tensile Strength |
| | days | % | lb./sq. in. | % | lb./sq. in. |
| In 1 per cent. sodium hydroxide solution | 1 | ±0·000 | 110 | ±0·000 | 130 |
| | 6 | +0·025 | 370 | +0·007 | 380 |
| | 11 | 0·027 | 400 | 0·027 | 190 |
| | 15 | 0·030 | 420 | 0·077 | 160 |
| | 22 | 0·035 | 400 | 0·218 | 110 |
| | 29 | 0·034 | 370 | 0·393 | 150 |
| | 36 | 0·036 | 400 | 0·513 | 150 |
| | 43 | 0·038 | 380 | 0·577 | 160 |
| | 57 | 0·040 | 440 | 0·677 | 180 |
| | 85 | 0·043 | 380 | 0·824 | 160 |
| | 113 | 0·043 | 430 | 0·923 | 170 |
| | 141 | 0·044 | 410 | 1·028 | 200 |
| | 169 | 0·037 | 360 | 1·090 | 150 |
| In water .. .. | 1 | ±0·000 | 150 | ±0·000 | 180 |
| | 6 | +0·002 | 310 | +0·001 | 300 |
| | 11 | 0·006 | 360 | 0·015 | 190 |
| | 15 | 0·011 | 340 | 0·033 | 120 |
| | 22 | 0·013 | 370 | 0·097 | 120 |
| | 29 | 0·012 | 380 | 0·150 | 110 |
| | 43 | 0·016 | 350 | 0·219 | 90 |
| | 57 | 0·016 | 340 | 0·240 | 110 |
| | 85 | 0·018 | 350 | 0·262 | 120 |
| | 113 | 0·021 | 330 | 0·275 | 90 |
| | 141 | 0·021 | 310 | 0·279 | 120 |
| | 169 | 0·021 | 360 | 0·278 | 130 |
| | 197 | 0·022 | 330 | 0·280 | 150 |

Conclusions are:—

(1) Mortars containing non-reactive aggregate neither expanded significantly nor showed any abnormal decreases in tensile strength during storage under any of the conditions used.

(2) The expansions of reactive aggregate mortars were of the same order as those shown in Table 2. The tensile strengths of all these mortars decreased abnormally.

Observations on the mortars showed:—

(1) Mortars containing non-reactive aggregate developed neither reaction spots nor cracks.

(2) Mortars containing reactive aggregate developed reaction spots and cracks.

(3) In all storage conditions, cracks, which were associated with reacted aggregate particles, were first observed six days after fabrication, when mortar expansions were less than 0·01 per cent. These cracks, which were short and fine when first observed, lengthened and widened as the opal particles reacted and expanded.

Other observations confirmed those given in section (i).

## 4. Discussion

It will be shown in later papers that expansion depends (other things being equal) on three variables, namely, the relative amounts of alkalis, reactive material, and uncombined water. Mortars stored in dry air and in moist air differ in their amounts of uncombined water; those stored in alkali solutions and in water contain larger amounts of uncombined water than those stored in dry air and in moist air. The alkali contents of mortars stored in dry air and in moist air remain constant whereas those of mortars stored in alkali solutions and in water can undergo significant changes. It should be remembered that the following discussion only concerns small mortar test pieces. It is probable that only the surface layer of large concrete specimens or structures would be similarly affected by environmental conditions.

Depending on the amount available, uncombined water has two opposing actions on the expansion of reacting opal. Firstly, the volume of a reacting opal particle increases as it absorbs water. Consequently, within certain limits, mortars should expand by amounts depending on their uncombined water contents. Secondly, as reacting opal absorbs water, the properties of the reaction product change from those of a solid (gel) to those of a liquid (sol). The sol has a negligible expansive effect compared with the gel. Thus, for mortars which contain large amounts of uncombined water, the change in properties of the reaction product is rapid and expansions are not as high as those of mortars which contain normal amounts of uncombined water.

Provided the concentration of alkalis in the storage water or solution is lower than that in the solution in the mortar, alkalis will diffuse from the mortar into the surrounding medium. Thus small mortar specimens stored in water are unlikely to expand excessively as the amount of reaction product formed is small because of the decrease in the amount of alkalis available for reaction. Furthermore, since the amount of available water in the mortar is high the reaction product should form a sol rather than a gel.

When the storage medium is a sodium hydroxide solution (potassium hydroxide solution should behave similarly) sodium and hydroxyl ions will pass into or out of the mortar, depending on whether the concentration of these ions in the storage solution is greater or less than that in the solution in the mortar. If the concentrations of ions in the storage solution and mortar solution are approximately equal, opal will be attacked at a rate equivalent to that in mortars stored in moist air. It does not follow, however, that mortars stored in alkali solutions will expand at a rate equivalent to those stored in moist air since in the former large amounts of uncombined water are available for absorption by reacting opal, and the reaction product should form a sol rather than a gel.

A feature of reactive aggregate mortars when stored in water or 1 per cent. sodium hydroxide solution is that some of the reaction product is deposited as a cloudy gel on the mortar surfaces, but since these cloudy gels, which are very soft, are unlikely to expand the mortar, they will not be considered further here.

All mortars which contained reacted aggregate particles were cracked, although the expansions of those stored in dry air were negative. These observations indicate that mortar deterioration cannot always be detected by length changes of test bars. Tensile strength changes, however, revealed that all mortars containing reacted aggregate had deteriorated.

Cracks produced in mortars stored in moist air, in 1 per cent. sodium hydroxide solution, and in water were caused by the reacting particles exerting disruptive swelling pressures on the mortar and not by drying shrinkage, since the cement in these mortars retained much of their excess mixing water. In mortars stored in dry air cracks and reduction in tensile strength were due to the combined effect of the slight swelling of reacted particles caused by the absorption of some water and of the shrinkage of hydrated cement as it lost water. Since these are opposing actions, the resultant cracking is equivalent to that produced by a slightly greater swelling of reacted particles in a similar mortar in which the cement does not shrink abnormally (i.e. mortars stored in moist air).

### 5. Summary of Conclusions

(i) Absorption of water by reacting opal particles caused mortar expansion. Removal of uncombined mixing water from mortar inhibited expansion.

(ii) Cracks, associated with reacted opal particles, were observed in mortars stored under all conditions used.

(iii) Cracks reduced the tensile strength of all reactive aggregate mortars.

# NOTES

## "Australian Journal of Scientific Research"

In collaboration with the Australian National Research Council, C.S.I.R. has completed arrangements for the establishment in Australia of a new journal, as a medium for the publication of research papers of outstanding merit, open to receive contributions from research workers irrespective of the organization to which they are attached.

The journal, to be known as the *Australian Journal of Scientific Research,* will be printed in two series, both to be issued quarterly in the first instance. It is expected that the first number of Series A (Physical Sciences) will be issued in March 1948, and the first number of Series B (Biological Sciences, including agriculture) in February 1948.

Dr. N. S. Noble has been appointed as Editor and is stationed at Head Office. Editorial policy will be decided by an Editorial Board under the Chairmanship of the Editor and comprising as members Professors W. J. Dakin, E. J. Hartung, L. H. Martin, and J. G. Wood.

It is intended to maintain a high standard of quality by adhering to a strict refereeing system, and while members of the Board may referee some papers themselves, it is intended that where necessary the services of outside referees will be called upon. It is obvious that there can be no absolute standard of quality, but, as a general guide, the Board has decided that papers to be acceptable for publication in the new journal should be of such a quality that they would be acceptable to specialist journals overseas.

It is intended that the Council's Bulletin series will continue, and that the present C.S.I.R. Journal will be issued throughout 1948 at least.

Papers intended for the new journal should be submitted to Dr. Noble at the Council's Head Office, 314 Albert-street, East Melbourne.

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## The United Nations Educational, Scientific and Cultural Organization

The present fashion for the extensive use of initials may well cause difficulties for students of philology in years to come. The growth of the United Nations and its satellite organizations has produced a heavy crop of new symbols representing the complicated, high-sounding titles of various new bodies. During November, the annual conference of UNESCO will be held at Mexico City, and in recent months there have been various references in the daily Press to this body. What is UNESCO? What are its aims and objects? How does it function? What is its significance to Australians and, in particular, to Australian scientists? The purpose of this article is to give a brief description of its history, its present organization and activities, and its plans for the future.

The United Nations Educational, Scientific, and Cultural Organization is one of the specialized agencies of the United Nations, reporting directly to the Economic and Social Council. It grew out of the

Conference of Allied Ministers of Education which met in London at regular intervals from 1942 to 1945 to plan for the reconstruction of the educational facilities of occupied Europe. It soon became clear that the problems in this field which would await solution when victory was achieved would be enormous, and it was thought that an international organization for education would be desirable. The planning of such an organization to undertake the reconstruction of educational and cultural facilities in Europe was therefore commenced, and the work was stimulated by the discussions at San Francisco in 1945 when the United Nations Charter was drawn up, and it was agreed that the promotion of international cultural and educational cooperation should be an objective of the United Nations. Following on this, the British and French Governments invited all Governments of the United Nations to be represented at a Conference in London in November 1945 to establish an appropriate international body.

Forty-four Governments were represented at this Conference, and it was agreed that a United Nations Educational, Scientific, and Cultural Organization should be established. (The original proposal had been for a United Nations Educational and Cultural Organization; the inclusion of the word Scientific in the title was agreed to at the Conference largely as a result of the missionary efforts of Dr. Joseph Needham, F.R.S., who, during the time he was in charge of the Sino-British Scientific Cooperation Office in Chungking, had campaigned vigorously for greater organization in international scientific cooperation.)

The purposes and functions of UNESCO, as defined briefly in the final act of the Conference, are as follows:—

". . . to contribute to peace and security by promoting collaboration among the nations through education, science, and culture in order to further universal respect for justice, for the rule of law, and for the human rights of the world, without distinction of race, sex, language, or religion, by the Charter of the United Nations."

Its functions are: (*a*) to collaborate in the work of advancing mutual knowledge and understanding of peoples, through all means of mass communication; (*b*) to give fresh impulse to popular education and to spread culture; and (*c*) to maintain, increase, and diffuse knowledge. But "with a view to preserving the independence, integrity, and fruitful diversity of the cultures and educational systems of the States members of UNESCO, the Organization is prohibited from intervening in matters which are essentially within their domestic jurisdiction." These are wide and ambitious functions!

The Organization envisaged by the Conference consists of a General Conference, an Executive Board, and a Secretariat. A Preparatory Commission was also set up by the Conference to make detailed arrangements for the establishment of the Organization. Sir Alfred Zimmern, formerly Professor of International Relations at Oxford, was appointed as Secretary-General of the Preparatory Commission, and on his resignation he was succeeded by Dr. Julian Huxley, the eminent biologist. The Preparatory Commission met in June 1946, and at the first General Conference in Paris in November 1946 UNESCO came formally into being, with its headquarters in Paris.

The Organization has thus been in existence just over a year, during which time progress has been made in the building up of its Secretariat and in the planning and initiation of its activities. The cumbersome structure of international organizations, which seems inescapable when a large number of separate nation States attempt to cooperate, tends to attract undue attention to constitutions, acts, and organizational arrangements at the expense of the actual work being undertaken. UNESCO is no exception, but let us attempt to examine what the Organization is actually doing or proposing to do.

Apart from organizational difficulties, its activities are obviously limited by its budget. The General Conference in Paris agreed to a total budget for the current year (1947) of $6,950,000. Of this, however, $950,000 was to meet costs incurred prior to 1947, leaving $6,000,000 for UNESCO activities in 1947, not a very large sum for such high functions. The programme finally adopted by the Executive Board falls into two main groups of activities:—

(*a*) Four large-scale projects of a comprehensive nature.

(*b*) Specialized activities within the fields of education, science and culture.

In the first group comes the reconstruction and rehabilitation of educational, scientific, and cultural life in countries devastated by war, a project of great urgency in Europe and parts of Asia—an urgency which it is hard to grasp in Australia which has emerged from the war physically unscathed. Active field work in this project is at present being undertaken in Czechoslovakia, Greece, Poland, and Yugoslavia, as well as in Italy and Austria. In cooperation with other agencies and organizations a world-wide campaign is in progress for the collection of contributions in money, materials, and services for distribution in the devastated areas.

The second large-scale project has the ambitious and long-range object of teaching the illiterates of the world (who number more than one-half of its population) to read and write, and simultaneously campaigning for provision of a basic minimum of education for all the peoples of the world. Linked with this is the third project, that of education for international understanding which is of a continuing character seeking to stimulate and assist the active study of international relations in all countries.

The fourth large-scale project is definitely a scientific one, consisting of a far-reaching programme of research into the needs and possibilities of the vast forested Amazon area, which comprises four million square miles in the heart of the South American continent. A team of scientists making preliminary investigations includes a tropical botanist, an expert on tropical diseases, and two anthropologists. Conversations are being held with the Governments of Brazil, Bolivia, Colombia, Ecuador, Peru, Venezuela, Great Britain, France, the Netherlands, and the United States to examine the possibilities of establishing an International Research Institute at the mouth of the Amazon River.

So much for the large-scale projects. The specialized activities within the fields of education and culture can only be mentioned here. They include a study of educational techniques, the coordination, standardization, and improvement of educational statistics, a study of the tensions affecting international understanding, a preliminary study of the international aspects of philosophy and humanistic studies

as they are related to UNESCO's objectives, projects in the fields of literature and the theatre, music and the visual arts, studies of the needs and resources of libraries and museums, and studies on the use of mass communication media—films, radio, and the press.

Natural sciences play a major role in the reconstruction and rehabilitation project, particularly in relation to scientific and technical schools, colleges, universities and research institutes in war-devastated areas. The major activity being undertaken, however, is the establishment of Field Science Cooperation Offices in parts of the world which are remote from the main centres of science and technology. The object of these offices is to facilitate contact between scientists and technologists in various parts of the world, to assist in the solution of problems of scientific literature, translation, and reprints, and to assist the exchange of scientific men in the areas concerned. They will also serve as reception and distribution centres for scientific information, particularly of problems indigenous to the region. In addition to the office already established in the Hylean Amazon (at Rio de Janeiro) two more offices are located in the Far East and the Middle East. It is hoped to set up an office in Southern Asia in 1948.

The Natural Sciences Division of UNESCO is also engaged on a study of scientific documentation and scientific work of international significance. It is collecting information on scientific apparatus and scientific cinema films, is preparing a world register of scientists, and is investigating means of facilitating the travel of scientists throughout the world. It is also providing assistance for the already established International Scientific Unions, in an attempt to stimulate their activities by removing some of the factors which have hindered their work in the past. Office accommodation and secretarial staff for the International Council of Scientific Unions has been provided at UNESCO House in Paris.

From this necessarily sketchy outline of UNESCO activities it will be seen that the Organization is definitely attempting a number of practical tasks within the framework of its objectives; indeed some criticism has already been voiced that it is attempting to do too much and that it would be better if it concentrated its activities, in the first instance at any rate, on a smaller number of projects. Whether or not this criticism is justified remains to be seen. Much will depend on the calibre of the staff recruited and on the support given by member States to its activities whether this " magnificent experiment in international understanding " succeeds. The most notable absentee from the list of members is the U.S.S.R., but most other members of the United Nations have joined. It is interesting to note that UNESCO is not the first attempt at international cooperation in the cultural field, as the League of Nations established an International Institute of Intellectual Cooperation, with many of its objects similar to those of UNESCO. This organization did not flourish, however. The main reasons for its failure would appear to have been lack of financial resources and also the fact that it was insufficiently executive and practical. The proposed organization for UNESCO should avoid the latter difficulties. Whether the first difficulty can be avoided will depend on the support which the member States are prepared to give it.

UNESCO has recommended that in each member State there should be National Cooperating Bodies to maintain liaison between it and the country concerned. In Australia, the formation of such bodies

has been entrusted to the Commonwealth Office of Education. This office is the pivot in Australia for all UNESCO activities and, as UNESCO develops its work, more and more information should be available. It is hoped that all scientists in Australia and others interested in UNESCO's work will be prepared to support the activities of the National Cooperating Bodies in as practical a way as possible, by providing publicity for the work of UNESCO. This should then help to ensure the Organization's success, by enabling the individual to take an active interest in, and give support to, its activities.

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## "Prevention of Deterioration Abstracts"

The National Research Council of the National Academy of Sciences (Prevention of Deterioration Center, Room 204), 2101 Constitution-avenue, Washington, D.C., can now offer the *Prevention of Deterioration Abstracts* on a yearly subscription basis. These Abstracts are set up under the following headings: biological agents; electrical and electronic equipment; fungicides and other toxic compounds; JAN Deterioration Prevention Committee; lacquers, paints and varnishes; leather; lubricants; metals; miscellaneous; optical instruments and photographic equipment; packaging and storage; plastics, resins, rubbers, and waxes; textiles and cordage; wood and paper. Items abstracted include journal articles, patents, specifications, unpublished reports prepared by various Army, Navy and other governmental groups, and unpublished British, Australian, and Canadian reports.

There will be approximately 1,500 pages of the Abstracts per year. The individual abstracts are in loose leaf form, so that they may be arranged in the manner desired by the individual receiving them. Throughout the calendar year, all the abstracts classified under any one heading will be numbered consecutively.

Comments made by the personnel of the Prevention of Deterioration Center are added to many of these abstracts. In the comments attempts are made to relate a specific report with other relevant ones, to evaluate reports, or to make suggestions concerning further needed research.

The price, which includes two binders and index guides, will be $37.50 per year. Two binders are required for one year's subscription. The fiscal year will be from July 1 to June 30. The Abstract series started in April 1946 and back issues may be obtained at the regular subscription price.

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## Reviews

### "Advances in Grassland Husbandry and Fodder Production: Second Symposium."

(Bulletin 38 of the Imperial Bureau of Pastures and Field Crops, Aberystwyth, Wales, June 1947. 84 pp. Price 6s. (sterling). Obtainable from the Central Sales Branch, Imperial Agricultural Bureaux, Penglais, Aberystwyth, Wales.)

Bulletin 32 was the first symposium in this series. The two bulletins are akin to the earlier "Herbage Reviews" series.

The bulletin opens with four articles and the remainder of the "symposium" is a series of summaries, in some instances lengthy, of eleven papers and reports of diverse origin and objective.

The first article on objectives in veld investigations in Southern Rhodesia by West and Rattray gives an excellent appreciation of the problems of veld management and the techniques to be used in the investigations. The similarity of environment to coastal and sub-coastal Queensland gives added interest to the Australian reader. A short article on the economics of ley farming by A. W. Ashby follows. This is mainly of local interest. Professor Travin's discussion on "Formation of Plant Species" is an aspect of geo-botany which is not commonly included in an agricultural botany publication. Travin deduces a correlation between the process of species formation and seismic and volcanic activity and associates new species formation with regions of young geo-synclines. The statistical data presented are not particularly convincing. The fourth article is on "Forage production in Switzerland"—a translation by Miss Roseveare from the German by Alfred Kauter. This article traces the intensification of cropping and sown pastures for a period of ten years including the war period, largely because of the urgency of increasing home food production. The methods adopted included intensive extension work and some measure of compulsory ploughing and cropping.

The summaries of papers follow and include two of Australian origin, Schofield's study of coastal pastures at South Johnstone, Queensland, and Andrew's report on pasture investigations in Victoria during 1944/45. The other nine summaries are on a Scottish method of grassland improvement, agricultural seed production as a new industry in Welsh farming, grassland research and advisory work in Sweden, birdsfoot trefoil as a forage legume, hay dehydration in the south-western United States, U.S. Regional Pasture Research Laboratory, weeds in Fiji, pastures and fodder plants in Sierra Leone, and land resources of Tripolitania.

The subjects of this bulletin are both interesting and valuable but it is scarcely a symposium; rather is it a review.

J. G. D.

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"Chemical Composition of Plants as an Index of Their Nutritional Status."

By D. W. Goodall, Ph.D., D.I.C., F.L.S., and F. G. Gregory, D.Sc., F.R.S.

(Technical Communication 17 of the Imperial Bureau of Horticulture and Plantation Crops, East Malling, Kent, England, July, 1947. Pp. 167, bibl. 936. Price 9s. (sterling). Obtainable from Imperial Agricultural Bureaux, Central Sales Branch, Penglais, Aberystwyth, Wales.)

This communication may be divided roughly into three parts, which deal respectively with (i) theoretical aspects of the relationship of yield to nutrition supply, and the effect of this on concentration of nutrients in the plant; (ii) detailed consideration of the methods and techniques of plant sampling and analysis, their application, and the possible interpretations of the results; (iii) the comparison of plant analysis with field trials, soil analysis, and the use of deficiency symptoms as methods of nutritional diagnosis.

The publication should be of considerable assistance to the present-day worker on plant problems who must decide such questions as: Are field trials or pot cultures most suitable? Will the symptoms revealed by plant injection tell a sufficient story or must they be

backed by soil analysis, and if soil analysis is used, are chemical or biological methods preferable? Will observation of weed flora or of obvious deficiency symptoms give the final answer or can that be revealed only by determination of the most minute trace element in the plant? What have the hundreds of previous workers with their different methods and different techniques achieved? What is the lesson of their experience? What do their data signify?

In addition to the comprehensive bibliography of over 900 entries, subject and author indexes are provided.

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## Recent Publications of the Council

Since the last issue of this *Journal,* the following publications of the Council have been issued:—

*Bulletin No.* 202.—"The Strain Complex and Symptom Variability of Tomato Spotted Wilt Virus," by D. O. Norris, M.Sc. (Agric.).

The great variation in symptoms produced by the spotted wilt virus has puzzled plant pathologists since the disease was first studied. The present work demonstrates that most of the variability within any one species is, in fact, due to the virus being not an entity but a complex of closely related strains. This is the fundamental cause of variation, but environment plays an important subsidiary part. There are at least five distinct strains, with symptoms varying in severity from a barely distinguishable mottle to complete necrosis.

A particular tomato plant may be infected by just one of these strains or by several different ones although commonly all five are present, the symptoms depending upon which strain predominates. The most severe strain, called the "tip-blight" strain, sometimes occurs on its own, when it produces a disease so severe that the young growing part of the plant is rapidly killed.

The tomato normally encourages the severe strains of the virus to multiply, but it might prove practicable to evolve a variety of tomato which would encourage only the milder strains of virus, thus reducing the severity of the disease to a point where it scarcely affects the yield.

*Bulletin No.* 206.—"Pedogenesis Following the Dissection of Lateritic Regions in Southern Australia," by C. G. Stephens, M.Sc.

This Bulletin deals with the genesis and relationships of soils found in the various lateritic regions of southern Australia. It is shown that the different soils in any such region are related to the various horizons of the original lateritic soil and its parent rock. In addition it is demonstrated that parallel relationships exist between the soils and the original lateritic soil profile for all regions. These relationships are discussed for a number of areas where soil surveys have been carried out, and a diagram illustrating the connexion of the various named soil types and other features with the lateritic profile and with one another is presented. The diagram provides a

key to the interpretation of the soil and topographical pattern in lateritic regions in southern Australia and hence is of importance in ensuring sound soil survey procedure and in relating such surveys to fertility aspects of agricultural production in the areas concerned.

*Bulletin No.* 218.—" Studies of the Physiology and Toxicology of Blowflies. 12. The Toxicity of DDT as a Contact and Stomach Poison for Larvae of *Lucilia cuprina.* 13. Insectary Tests of Repellents for the Australian Sheep Blowfly," by D. F. Waterhouse, M.Sc.

Tests described in this Bulletin show that, although DDT is not a particularly effective contact insecticide against prepupae, it is highly toxic in low concentrations when ingested, particularly by young larvae. It did not appear to produce any of the symptoms of nervous system distress which are so typical of its effect on adult blowflies and many other insects. The results indicate that if DDT were incorporated in a blowfly dressing it would be highly toxic to newly hatched larvae but older larvae would be less affected and eggs not at all.

In the tests of repellents, various essential oils and other materials were applied to sheep in an insectary to test their efficiency in preventing oviposition by *Lucilia cuprina.* The test materials were applied in a ring around cotton wool plugs, which had been soaked in an attractive solution and tied in the fleece. The repellent effect of Ceylon citronella oil was confirmed, but Java oil was not repellent. The oils of *Zieria smithii* and Huon pine were repellent, while oils from the leaf and wood of white cypress pine were ineffective. Of five eucalyptus oils, three were not repellent and two were attractive. Chemically pure oleic acid was repellent, while a commercial grade was not. Two materials containing indalone were effective repellents, as were also dimethyl phthalate and 612.

" The Commercial Timbers of Australia—Their Properties and Uses," by I. H. Boas, M.Sc.

This book is divided into two parts. The first deals with the general technology of the timbers and discusses wood structure, including various forms of timber defect, the mechanical and physical properties of timbers, methods of seasoning, preservative treatment and durability, the bending of wood, grading, veneer and plywood, improved wood, the manufacture of paper from Australian hardwoods, and Australian essential oils.

The second part of the book lists the individual timbers, and gives the characteristics of each, including their density, the amount of shrinkage that can be expected, their durability, the seasoning required, main uses, and the availability of the timber. To aid in the selection of suitable timbers for specific purposes, the articles for which wood is commonly used are listed and the timbers that can be employed for each are given. A comprehensive bibliography dealing with Australian timbers is included, and the whole book has been carefully indexed.

(This book is not being distributed by C.S.I.R., but copies are obtainable from Tait Book Co. Pty. Ltd., 349 Collins-street, Melbourne. Price 12s. 6d., postage 8d.)

## Forthcoming Publications of the Council.

At the present time, the following future publications of the Council are in the press:—

*Bulletin No.* 210.—"Preliminary Survey of the Natural Pastures of the New England District of New South Wales, and a General Discussion of Their Problems," by R. Roe, B.Sc. (Agric.).

*Bulletin No.* 212.—"The Frictional Properties of Lead-Base and Tin-Base Bearing Alloys: The Role of the Matrix and the Hard Particles," by D. Tabor, Ph.D.

*Bulletin No.* 213.—"Laboratory and Field Tests of Mosquito Repellents," by R. N. McCulloch, B.Sc., B.Sc.Agr., and D. F. Waterhouse, M.Sc.

*Bulletin No.* 214.—"The Preparation and Properties of Synthetic Cryolite," by P. Dixon, M.Sc., and T. R. Scott, M.Sc.

*Bulletin No.* 215.—"Studies in the Biology of the Skin and Fleece of Sheep. 4. The Hair Follicle Group and its Topographical Variations in the Skin of the Merino Fœtus," by H. B. Carter, B.V.Sc., and Margaret H. Hardy, M.Sc.

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